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Volume XV

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1. Good operating practices;
2. Directions on how to assess performance and to qualify data;
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4. Directions to permit design of auditing activities.

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GUIDELINES FOR DEVELOPMENT OF A QUALITY ASSURANCE PROGRAM: VOLUME XV - DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES BY CONTINUOUS MONITORS

by

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ABSTRACT

Guidelines for the quality control of the continuous measurement of sulfur dioxide emissions by Performance Specification 2 are presented. These include:

1. Good operating practices;
2. Directions on how to assess performance and to qualify data;
3. Directions on how to identify trouble and to improve data quality;
4. Directions to permit design of auditing activities.

The document is not a research report. It is designed for use by operating personnel.

This work was submitted in partial fulfillment of contract Durham 68-02-1234 by Research Triangle Institute under the Sponsorship of the Environmental Protection Agency. Work was completed as of January, 1976.

1.0 INTRODUCTION

1.0 INTRODUCTION

This document presents guidelines for implementing a quality assurance program for the measurement of sulfur dioxide emissions from stationary sources by continuous monitors.

The objectives of this quality assurance program are to:

1. Provide routine indications for operating purposes of satisfactory performance of personnel and/or equipment,
2. Provide for prompt detection and correction of conditions that contribute to the collection of poor quality data,
3. Collect and supply information necessary to describe the quality of the data.

To accomplish the above objectives, a quality assurance program must contain the following components:

1. Routine training and/or evaluation of operators,
2. Routine monitoring of the variables and/or parameters which may have a significant effect on data quality,
3. Development of techniques to detect defects,
4. Development of methods to qualify data,
5. Action strategies to increase the level of precision in the reported data and/or to detect equipment defects or degradation and to correct same.

Implementation of a quality assurance program will result in data that are more preferable in terms of precision and accuracy and will enable the monitoring network to continuously generate data of acceptable quality.

This document is divided into three sections, as follows:

1. 1.0 INTRODUCTION--This section lists the overall objectives of a quality assurance program and delineates the program components necessary to accomplish the given objectives.
2. 2.0 DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES BY CONTINUOUS MONITORS--This section includes the method description, plan activity matrix, operational procedures, and auditing procedures. Subsection numbering is consistent with section 5.11 of a larger document, The Quality Assurance Handbook for Air Pollution Measurements, Volume III, Stationary Sources Specific Methods.
3. 3.0 FUNCTIONAL ANALYSIS--This section includes an estimate of the precisions and biases of the various measurement components which collectively comprise the continuous monitoring method, and an estimate of the total precision and bias of the method.

2.0 DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES BY CONTINUOUS MONITORS*

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* The numbering in this section is consistent with section 5.11 of a larger document, The Quality Assurance Handbook for Air Pollution Measurements, Vol. III--Stationary Sources Specific Methods.

5.11 DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES BY CONTINUOUS MONITORS

This section describes a quality control/quality assurance program designed specifically to ensure that sulfur dioxide data generated from continuous stack monitoring systems is of acceptable quality. To present the program, the section has been divided into the following subsections:

5.11.1 Performance Specification 2,
5.11.2 Plan Activity Matrix,
5.11.3 Operational Procedures, and
5.11.4 Auditing Procedures.

A reprint of "Performance Specification 2--Performance Specifications and Specification Test Procedures for Monitors of SO_2 and NO_x from Stationary Sources" is included in section 5.11.1 for convenient reference. The equipment specifications and procedural guidelines detailed in this quality assurance document were based on statements made in the Performance Specification 2. The scope of this document, however, does not include discussions concerning oxides of nitrogen monitors even though they are covered in Performance Specification 2. Also contained in section 5.11.1 is a block diagram which delineates the procedures for continuously measuring sulfur dioxide emissions.

The Plan Activity Matrix in section 5.11.2 includes the characteristic checks for each of the operating procedures. The operating procedures themselves are described in some detail in section 5.11.3. The audit procedures described in section 5.11.4 provide a basis for assessing the performance in each operational category.

The method described in this document for the measurement of sulfur dioxide emissions can be broken down into the following series of operational categories:

1. Definition of monitoring requirements and system hardware,
2. Installation and testing,
3. Preventive maintenance and routine testing.

Within each category both routine and nonroutine procedures are required. The routine procedures form the basic criteria for monitoring sulfur dioxide at a given stack and obtaining data. The nonroutine procedures provide characteristic checks for each of the routine procedures to insure that valid data will be ultimately collected from the system and to properly assess the quality of that data. Such nonroutine procedures are elements of an internal quality assurance or quality control program. The audit procedures are elements of an external quality assurance program (sometimes referred to simply as quality assurance). The purpose of section 5.11 is to provide the user with guidelines for developing quality control and quality assurance programs for a given source monitoring system.

5.11.1 Performance Specification

PERFORMANCE SPECIFICATION 2--PERFORMANCE SPECIFICATIONS AND SPECIFICATION TEST PROCEDURES FOR MONITORS OF SO_2 AND NO_x FROM STATIONARY SOURCES*

Reproduced from Appendix B, "Performance Specifications," of 40 CFR Part 60, Federal Register, Volume 40, Number 194; Monday, October 6, 1975.

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* Only the determination of sulfur dioxide (SO_2) emissions by continuous monitors are discussed in this quality assurance document.

5.11.1.1 Principle and Applicability

1. Principle and Applicability.

1.1 Principle. The concentration of sulfur dioxide or oxides of nitrogen pollutants in stack emissions is measured by a continuously operating emission measurement system. Concurrent with operation of the continuous monitoring system, the pollutant concentrations are also measured with reference methods (Appendix A). An average of the continuous monitoring system data is computed for each reference method testing period and compared to determine the relative accuracy of the continuous monitoring system. Other tests of the continuous monitoring system are also performed to determine calibration error, drift, and response characteristics of the system.

1.2 Applicability. This performance specification is applicable to evaluation of continuous monitoring systems for measurement of nitrogen oxides or sulfur dioxide pollutants. These specifications contain test procedures, installation requirements, and data computation procedures for evaluating the acceptability of the continuous monitoring systems.

5.11.1.2 Apparatus

2. Apparatus.

2.1 Calibration Gas Mixtures. Mixtures of known concentrations of pollutant gas in a diluent gas shall be prepared. The pollutant gas shall be sulfur dioxide or the appropriate oxide(s) of nitrogen specified by paragraph 6 and within subparts. For sulfur dioxide gas mixtures, the diluent gas may be air or nitrogen. For nitric oxide (NO) gas mixtures, the diluent gas shall be oxygen-free (<10 ppm) nitrogen, and for nitrogen dioxide (NO_2) gas mixtures the diluent gas shall be air. Concentrations of approximately 50 percent and 90 percent of span are required. The 90 percent gas mixture is used to set and to check the span and is referred to as the span gas.

2.2 Zero Gas. A gas certified by the manufacturer to contain less than 1 ppm of the pollutant gas or ambient air may be used.

2.3 Equipment for measurement of the pollutant gas concentration using the reference method specified in the applicable standard.

2.4 Data Recorder. Analog chart recorder or other suitable device with input voltage range compatible with analyzer system output. The resolution of the recorder's data output shall be sufficient to allow completion of the test procedures within this specification.

2.5 Continuous monitoring system for SO_2 or NO_x pollutants as applicable.

5.11.1.3 Definitions

3. Definitions.

3.1 Continuous Monitoring System. The total equipment required for the determination of a pollutant gas concentration in a source effluent. Continuous monitoring systems consist of major subsystems as follows:

3.1.1 Sampling Interface—That portion of an extractive continuous monitoring system that performs one or more of the following operations: acquisition, transportation, and conditioning of a sample of the source effluent or that portion of an in-situ continuous monitoring system that protects the analyzer from the effluent.

3.1.2 Analyzer—That portion of the continuous monitoring system which senses the pollutant gas and generates a signal output that is a function of the pollutant concentration.

3.1.3 Data Recorder—That portion of the continuous monitoring system that provides a permanent record of the output signal in terms of concentration units.

3.2 Span. The value of pollutant concentration at which the continuous monitoring system is set to produce the maximum data display output. The span shall be set at the concentration specified in each applicable subpart.

3.3 Accuracy (Relative). The degree of correctness with which the continuous monitoring system yields the value of gas concentration of a sample relative to the value given by a defined reference method. This accuracy is expressed in terms of error, which is the difference between the paired concentration measurements expressed as a percentage of the mean reference value.

3.4 Calibration Error. The difference between the pollutant concentration indicated by the continuous monitoring system and the known concentration of the test gas mixture.

3.5 Zero Drift. The change in the continuous monitoring system output over a stated

5.11.1.3 Definitions (continued)

period of time of normal continuous operation when the pollutant concentration at the time for the measurements is zero.

3.6 Calibration Drift. The change in the continuous monitoring system output over a stated time period of normal continuous operations when the pollutant concentration at the time of the measurements is the same known upscale value.

3.7 Response Time. The time interval from a step change in pollutant concentration at the input to the continuous monitoring system to the time at which 95 percent of the corresponding final value is reached as displayed on the continuous monitoring system data recorder.

3.8 Operational Period. A minimum period of time over which a measurement system is expected to operate within certain performance specifications without unscheduled maintenance, repair, or adjustment.

3.9 Stratification. A condition identified by a difference in excess of 10 percent between the average concentration in the duct or stack and the concentration at any point more than 1.0 meter from the duct or stack wall.

5.11.1.4 Installation Specifications

4. Installation Specifications. Pollutant continuous monitoring systems (SO_2 and NO_x) shall be installed at a sampling location where measurements can be made which are directly representative (4.1), or which can be corrected so as to be representative (4.2) of the total emissions from the affected facility. Conformance with this requirement shall be accomplished as follows:

4.1 Effluent gases may be assumed to be nonstratified if a sampling location eight or more stack diameters (equivalent diameters) downstream of any air in-leakage is selected. This assumption and data correction procedures under paragraph 4.2.1 may not be applied to sampling locations upstream of an air preheater in a stream generating facility under Subpart D of this part. For sampling locations where effluent gases are either demonstrated (4.3) or may be assumed to be nonstratified (eight diameters), a point (extractive systems) or path (in-situ systems) of average concentration may be monitored.

4.2 For sampling locations where effluent gases cannot be assumed to be nonstratified (less than eight diameters) or have been shown under paragraph 4.3 to be stratified, results obtained must be consistently representative (e.g. a point of average concentration may shift with load changes) or the data generated by sampling at a point (extractive systems) or across a path (in-situ systems) must be corrected (4.2.1 and 4.2.2) so as to be representative of the total emissions from the affected facility. Conformance with this requirement may be accomplished in either of the following ways:

4.2.1 Installation of a diluent continuous monitoring system (O_2 or CO_2 as applicable) in accordance with the procedures under paragraph 4.2 of Performance Specification 3 of this appendix. If the pollutant and diluent monitoring systems are not of the same type (both extractive or both in-situ), the extractive system must use a multipoint probe.

4.2.2 Installation of extractive pollutant monitoring systems using multipoint sampling probes or in-situ pollutant monitoring systems that sample or view emissions which are consistently representative of the total emissions for the entire cross section. The Administrator may require data to be submitted to demonstrate that the emissions sampled or viewed are consistently representative for several typical facility process operating conditions.

4.3 The owner or operator may perform a traverse to characterize any stratification of effluent gases that might exist in a stack or duct. If no stratification is present, sampling procedures under paragraph 4.1 may be applied even though the eight diameter criteria is not met.

4.4 When single point sampling probes for extractive systems are installed within the stack or duct under paragraphs 4.1 and 4.2.1, the sample may not be extracted at any point less than 1.0 meter from the stack or duct wall. Multipoint sampling probes installed under paragraph 4.2.2 may be located at any points necessary to obtain consistently representative samples.

5.11.1.5 Continuous Monitoring System Performance Specifications

5. Continuous Monitoring System Performance Specifications.

The continuous monitoring system shall meet the performance specifications in Table 2-1 to be considered acceptable under this method.

5.11.1.5 Continuous Monitoring System Performance Specifications

TABLE 2-1.—*Performance specifications*

Parameter	*Specification*
1. Accuracy [1]	≤20 pct of the mean value of the reference method test data.
2. Calibration error [1]	≤ 5 pct of each (50 pct, 90 pct) calibration gas mixture value.
3. Zero drift (2 h) [1]	2 pct of span
4. Zero drift (24 h) [1]	Do.
5. Calibration drift (2 h) [1]	Do.
6. Calibration drift (24 h) [1]	2.5 pct. of span
7. Response time	15 min maximum.
8. Operational period	168 h minimum.

[1] Expressed as sum of absolute mean value plus 95 pct confidence interval of a series of tests.

5.11.1.6 Performance Specification Test Procedures

6. Performance Specification Test Procedures. The following test procedures shall be used to determine conformance with the requirements of paragraph 5. For NO_x anrequirements of paragraph 5. For NO_x analyzers that oxidize nitric oxide (NO) to nitrogen dioxide (NO_2), the response time test under paragraph 6.3 of this method shall be performed using nitric oxide (NO) span gas. Other tests for NO_x continuous monitoring systems under paragraphs 6.1 and 6.2 and all tests for sulfur dioxide systems shall be performed using the pollutant span gas specified by each subpart.

6.1 Calibration Error Test Procedure. Set up and calibrate the complete continuous monitoring system according to the manufacturer's writen instructions. This may be accomplished either in the laboratory or in the field.

6.1.1 Calibration Gas Analyses. Triplicate analyses of the gas mixtures shall be performed within two weeks prior to use using Reference Methods 6 for SO_2 and 7 for NO_x. Analyze each calibration gas mixture (50%, 90%) and record the results on the example sheet shown in Figure 2-1. Each sample test result must be within 20 percent of the averaged result or the tests shall be repeated. This step may be omitted for non-extractive monitors where dynamic calibration gas mixtures are not used (6.1.2).

6.1.2 Calibration Error Test Procedure. Make a total of 15 nonconsecutive measurements by alternately using zero gas and each caliberation gas mixture concentration (e.g., 0%, 50%, 0%, 90%, 50%, 90%, 50%, 0%, etc.). For nonextractive continuous monitoring systems, this test procedure may be performed by using two or more calibration gas cells whose concentrations are certified by the manufacturer to be functionally equivalent to these gas concentrations. Convert the continuous monitoring system output readings to ppm and record the results on the example sheet shown in Figure 2-2.

6.2 Field Test for Accuracy (Relative), Zero Drift, and Calibration Drift. Install and operate the continuous monitoring system in accordance with the manufacturer's written instructions and drawings as follows:

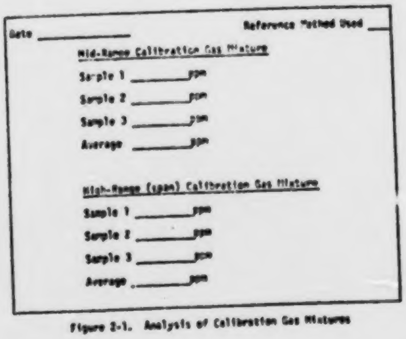
6.2.1 Conditioning Period. Offset the zero setting at least 10 percent of the span so that negative zero drift can be quantified. Operate the system for an initial 168-hour conditioning period in normal operating manner.

6.2.2 Operational Test Period. Operate the continuous monitoring system for an additional 168-hour period retaining the zero offset. The system shall monitor the source effluent at all times except when being zeroed, calibrated, or backpurged.

6.2.2.1 Field Test for Accuracy (Relative). For continuous monitoring systems employing extractive sampling, the probe tip for the continuous monitoring system and the probe tip for the Reference Method sampling train should be placed at adjacent locations in the duct. For NO_x continuous monitoring systems, make 27 NO_x concentration measurements, divided into nine sets, using the applicable reference method. No more than one set of tests, consisting of three individual measurements, shall be performed in any one hour. All individual measurements of each set shall be performed concurrently, or within a three-minute interval and the results averaged. For SO_2 continuous monitoring systems, make nine SO_2 concentration measurements using the applicable reference method. No more than one measurement shall be performed in any one hour. Record the reference method test data and the continuous monitoring system concentrations on the example data sheet shown in Figure 2-3.

6.2.2.2 Field Test for Zero Drift and Calibration Drift. For extractive systems, determine the values given by zero and span gas pollutant concentrations at two-hour intervals until 15 sets of data are obtained. For nonextractive measurement systems, the zero value may be determined by mechanically producing a zero condition that provides a system check of the analyzer internal mirrors and all electronic circuitry including the radiation source and detector assembly or by inserting three or more calibration gas cells and computing the zero point from the upscale measurements. If this latter technique is used, a graph(s) must be retained by the owner or operator for each measurement system that shows the relationship between the upscale measurements and the zero point. The span of the system shall be checked by using a calibration gas cell certified by the manufacturer to be functionally equivalent to 50 percent of span concentration. Record the zero and span measurements (or the computed zero drift) on the example data sheet shown in Figure 2-4. The two-hour periods over which measurements are conducted need not be consecutive but may not overlap. All measurements required under this paragraph may be conducted concurrent with tests under paragraph 6.2.2.1.

5.11.1.6 Performance Specifications Test Procedures (continued)



Date ____________ Reference Method Used ____

Mid-Range Calibration Gas Mixture

Sample 1 ________ppm

Sample 2 ________ppm

Sample 3 ________ppm

Average ________ppm

High-Range (span) Calibration Gas Mixture

Sample 1 ________ppm

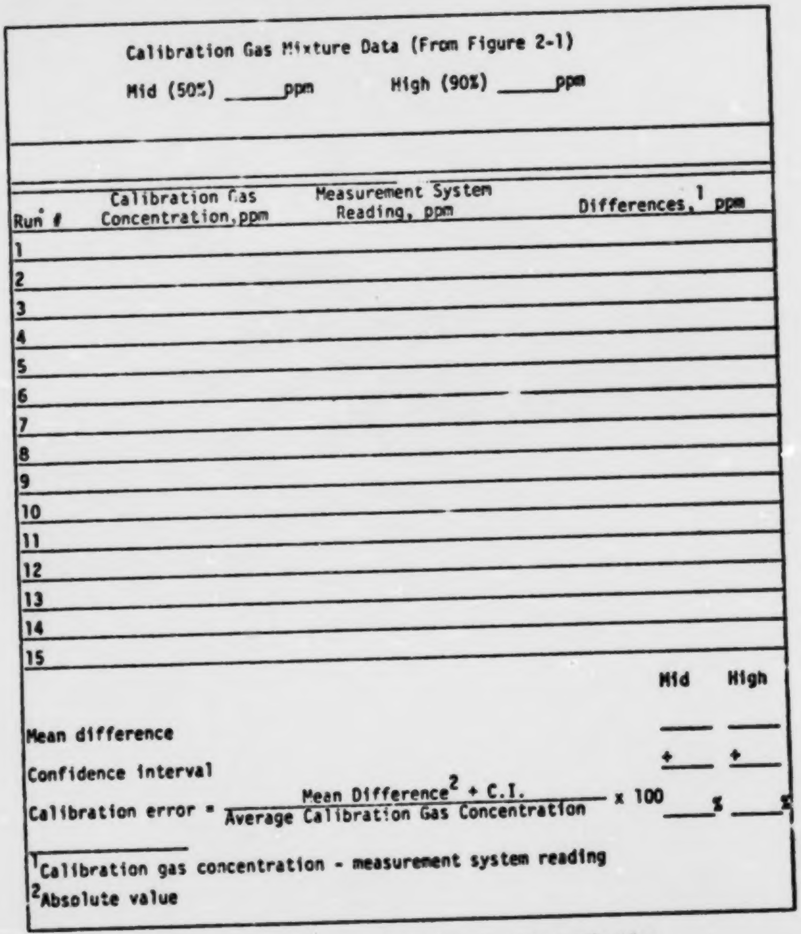
Sample 2 ________ppm

Sample 3 ________ppm

Average ________ppm

Figure 2-1. Analysis of Calibration Gas Mixtures

RULES AND REGULATIONS



Calibration Gas Mixture Data (From Figure 2-1)

Mid (50%) _____ppm High (90%) _____ppm

Run #	Calibration Gas Concentration, ppm	Measurement System Reading, ppm	Differences,[1] ppm
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			
13			
14			
15			

	Mid	High
Mean difference	____	____
Confidence interval	± ____	± ____
Calibration error = $\frac{\text{Mean Difference}^2 + \text{C.I.}}{\text{Average Calibration Gas Concentration}} \times 100$	____%	____%

---

[1] Calibration gas concentration - measurement system reading

[2] Absolute value

Figure 2-2. Calibration Error Determination

5.11.1.6 Performance Specifications Test Procedure (continued)

Test No.	Date and Time	Reference Method Samples					Analyzer 1-Hour Average (ppm)*		Difference (ppm)	
		SO_2 Sample 1 (ppm)	NO_x Sample 1 (ppm)	NO_x Sample 2 (ppm)	NO_x Sample 3 (ppm)	NO_x Sample Average (ppm)	SO_2	NO_x	SO_2	NO_x
1										
2										
3										
4										
5										
6										
7										
8										
9										

Mean reference method test value (SO_2) ______

Mean reference method test value (NO_x) ______

Average of the differences ______

Mean differences** = ______ ppm (SO_2), = ______ ppm (NO_x).

95% Confidence intervals = ± ______ ppm (SO_2), = ± ______ ppm (NO_x).

Accuracies = $\frac{\text{Mean difference (absolute value) + 95\% confidence interval}}{\text{Mean reference method value}}$ x 100 = ____% (SO_2), = ____% (NO_x).

* Explain and report method used to determine integrated averages.

** Mean differences = the average of the differences minus the mean reference method test value.

Figure 2-3. Accuracy Determination (SO_2 and NO_x)

Data Set No.	Time Begin	Time End	Date	Zero Reading	Zero Drift (ΔZero)	Span Reading	Span Drift (ΔSpan)	Calibration Drift (ΔSpan- Zero)
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
11								
12								
13								
14								
15								

Zero Drift = [Mean Zero Drift* ______ + CI (Zero) ______] ÷ [Span] x 100 = ______.
Calibration Drift = [Mean Span Drift* ______ + CI (Span) ______] ÷ [Span] x 100 = ______.
*Absolute Value.

Figure 2-4. Zero and Calibration Drift (2 Hour)

6.2.2.3 Adjustments. Zero and calibration corrections and adjustments are allowed only at 24-hour intervals or at such shorter intervals as the manufacturer's written instructions specify. Automatic corrections made by the measurement system without operator intervention or initiation are allowable at any time. During the entire 168-hour operational test period, record on the example sheet shown in Figure 2-5 the values given by zero and span gas pollutant concentrations before and after adjustment at 24-hour intervals.

6.3 Field Test for Response Time.

6.3.1 Scope of Test. Use the entire continuous monitoring system as installed, including sample transport lines if used. Flow rates, line diameters, pumping rates, pressures (do not allow the pressurized calibration gas to change the normal operating pressure in the sample line), etc., shall be at the nominal values for normal operation as specified in the manufacturer's written instructions. If the analyzer is used to sample more than one pollutant source (stack), repeat this test for each sampling point.

6.3.2 Response Time Test Procedure. Introduce zero gas into the continuous monitoring system sampling interface or as close to the sampling interface as possible. When the system output reading has stabilized, switch quickly to a known concentration of pollutant gas. Record the time from concentration switching to 95 percent of final stable response. For non-extractive monitors, the highest available calibration gas concentration shall be switched into and out of the sample path and response times recorded. Perform this test sequence three (3) times. Record the results of each test on the example sheet shown in Figure 2-6.

Date and Time	Zero Reading	Zero Drift (ΔZero)	Span Reading (After zero adjustment)	Calibration Drift (ΔSpan)

Zero Drift = [Mean Zero Drift* ________ + C.I. (Zero) ________]

÷ [Instrument Span] x 100 = __________.

Calibration Drift = [Mean Span Drift* ________ + C.I. (Span) ________]

÷ [Instrument Span] x 100 = __________.

* Absolute value

Figure 2-5. Zero and Calibration Drift (24-hour)

5.11.1.6 Performance Specification Test Procedures (continued)

Date of Test ____________

Span Gas Concentration ________ppm

Analyzer Span Setting ________ppm

Upscale
1 ________seconds
2 ________seconds
3 ________seconds

Average upscale response ________seconds

Downscale
1 ________seconds
2 ________seconds
3 ________seconds

Average downscale response ______seconds

System average response time (slower time) = _______seconds.

$$\%\text{deviation from slower system average response} = \left[\frac{\text{average upscale minus average downscale}}{\text{slower time}}\right] \times 100\% = \_\_\_\_.$$

Figure 2-6. Response Time

5.11.1.7 Calculations, Data Analysis, and Reporting

7. Calculations, Data Analysis and Reporting.

7.1 Procedure for determination of mean values and confidence intervals.

7.1.1 The mean value of a data set is calculated according to equation 2-1.

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i \qquad \text{Equation 2-1}$$

where:

x_i = absolute value of the measurements,
Σ = sum of the individual values,
$\bar{x}$ = mean value, and
n = number of data points.

7.1.2 The 95 percent confidence interval (two-sided) is calculated according to equation 2-2:

$$C.I._{95} = \frac{t_{.975}}{n\sqrt{n-1}} \sqrt{n(\Sigma x_i^2) - (\Sigma x_i)^2} \qquad \text{Equation 2-2}$$

where:

Σx_i = sum of all data points,
$t_{.975} = t_1 - \alpha/2$, and
$C.I._{95}$ = 95 percent confidence interval estimate of the average mean value.

Values for $t_{.975}$

	$t_{.975}$
1	12.706
2	4.303
3	3.182
4n	2.776
5	2.571
6	2.447
7	2.365
8	2.306
9	2.262
10	2.228
12	2.201
13	2.179
14	2.160
15	2.145
16	2.131

The values in this table are already corrected for n-1 degrees of freedom. Use n equal to the number of samples as data points.

7.2 Data Analysis and Reporting.

7.2.1 Accuracy (Relative). For each of the nine reference method test points, determine the average pollutant concentration reported by the continuous monitoring system. These average concentrations shall be determined from the continuous monitoring system data recorded under 7.2.2 by integrating or averaging the pollutant concentrations over each of the time intervals concurrent with each reference method testing period. Before proceeding to the next step, determine the basis (wet or dry) of the continuous monitoring system data and reference method test data concentrations. If the bases are not consistent, apply a moisture correction to either reference method concentrations or the continuous monitoring system concentrations as appropriate. Determine the correction factor by moisture tests concurrent with the reference method testing periods. Report the moisture test method and the correction procedure employed. For each of the nine test runs determine the difference for each test run by subtracting the respective reference method test concentrations (use average of each set of three measurements for NO_x) from the continuous monitoring system integrated or averaged concentrations. Using these data, compute the mean difference and the 95 percent confidence interval of the differences (equations 2-1 and 2-2). Accuracy is reported as the sum of the absolute value of the mean difference and the 95 percent confidence interval of the differences expressed as a percentage of the mean reference method value. Use the example sheet shown in Figure 2-3.

7.2.2 Calibration Error. Using the data from paragraph 6.1, subtract the measured pollutant concentration determined under

5.11.1.7 Calculations, Data Analysis, and Reporting (Continued)

paragraph 6.1.1 (Figure 2-1) from the value shown by the continuous monitoring system for each of the five readings at each concentration measured under 6.1.2 (Figure 2-2). Calculate the mean of these difference values and the 95 percent confidence intervals according to equations 2-1 and 2-2. Report the calibration error (the sum of the absolute value of the mean difference and the 95 percent confidence interval) as a percentage of each respective calibration gas concentration. Use example sheet shown in Figure 2-2.

7.2.3 Zero Drift (2-hour). Using the zero concentration values measured each two hours during the field test, calculate the differences between consecutive two-hour readings expressed in ppm. Calculate the mean difference and the confidence interval using equations 2-1 and 2-2. Report the zero drift as the sum of the absolute mean value and the confidence interval as a percentage of span. Use example sheet shown in Figure 2-4.

7.2.4 Zero Drift (24-hour). Using the zero concentration values measured every 24 hours during the field test, calculate the differences between the zero point after zero adjustment and the zero value 24 hours later just prior to zero adjustment. Calculate the mean value of these points and the confidence interval using equations 2-1 and 2-2. Report the zero drift (the sum of the absolute mean and confidence interval) as a percentage of span. Use example sheet shown in Figure 2-5.

7.2.5 Calibration Drift (2-hour). Using the calibration values obtained at two-hour intervals during the field test, calculate the differences between consecutive two-hour readings expressed as ppm. These values should be corrected for the corresponding zero drift during that two-hour period. Calculate the mean and confidence interval of these corrected difference values using equations 2-1 and 2-2. Do not use the differences between non-consecutive readings. Report the calibration drift as the sum of the absolute mean and confidence interval as a percentage of span. Use the example sheet shown in Figure 2-4.

7.2.6 Calibration Drift (24-hour). Using the calibration values measured every 24 hours during the field test, calculate the differences between the calibration concentration reading after zero and calibration adjustment, and the calibration concentration reading 24 hours later after zero adjustment but before calibration adjustment. Calculate the mean value of these differences and the confidence interval using equations 2-1 and 2-2. Report the calibration drift (the sum of the absolute mean and confidence interval) as a percentage of span. Use the example sheet shown in Figure 2-5.

7.2.7 Response Time. Using the charts from paragraph 6.3, calculate the time interval from concentration switching to 95 percent to the final stable value for all upscale and downscale tests. Report the mean of the three upscale test times and the mean of the three downscale test times. The two average times should not differ by more than 15 percent of the slower time. Report the slower time as the system response time. Use the example sheet shown in Figure 2-6.

7.2.8 Operational Test Period. During the 168-hour performance and operational test period, the continuous monitoring system shall not require any corrective maintenance, repair, replacement, or adjustment other than that clearly specified as required in the operation and maintenance manuals as routine and expected during a one-week period. If the continuous monitoring system operates within the specified performance parameters and does not require corrective maintenance, repair, replacement or adjustment other than as specified above during the 168-hour test period, the operational period will be successfully concluded. Failure of the continuous monitoring system to meet this requirement shall call for a repetition of the 168-hour test period. Portions of the test which were satisfactorily completed need not be repeated. Failure to meet any performance specifications shall call for a repetition of the one-week performance test period and that portion of the testing which is related to the failed specification. All maintenance and adjustments required shall be recorded. Output readings shall be recorded before and after all adjustments.

5.11.1.8 References

8. References.

8.1 "Monitoring Instrumentation for the Measurement of Sulfur Dioxide in Stationary Source Emissions," Environmental Protection Agency, Research Triangle Park, N.C., February 1973.

8.2 "Instrumentation for the Determination of Nitrogen Oxides Content of Stationary Source Emissions," Environmental Protection Agency, Research Triangle Park, N.C., Volume 1, APTD-0847, October 1971; Volume 2, APTD-0942, January 1972.

8.3 "Experimental Statistics," Department of Commerce, Handbook 91, 1963, pp. 3-31, paragraphs 3-3.1.4.

8.4 "Performance Specifications for Stationary-Source Monitoring Systems for Gases and Visible Emissions," Environmental Protection Agency, Research Triangle Park, N.C., EPA-650/2-74-013, January 1974.

5.11.1.9 Quality Control Program Specifications--

5.11.1.9.1 Quality control programs--purpose. Each laboratory and field station shall maintain a quality control program consistent with the procedures described in this manual. Such programs shall be designed to assure the quality and scientific reliability of laboratory and field data used in EPA activities and documents.

5.11.1.9.2 Quality control program--provisions. Each quality control program shall contain provisions for the management of data quality, which shall include the following:

1. Requirements for the production of quality control data and the use of quality control records;
2. Control of technical documents, testing methods, and calibration instructions, and changes thereto;
3. Control and calibration of test and analytical instruments and equipment used in certification testing;
4. Control of purchased equipment to include checks for analyzer conformance to specifications and continuing surveillance of that conformance;
5. Audit of routine calibration and preventive maintenance schedules;
6. Establishment of an organizational structure to carry out these provisions.

The intralaboratory quality control program shall provide for the establishment and maintenance of total quality control systems to assure continued precision and accuracy of the instrument data including, as appropriate, requirements for:

1. The checks and audits listed in table 5.11.1,
2. Routine use of an appropriate reference method (either Method 6 or 8) for replicate test data,

Table 5.11.1 Methods of monitoring variables

	Variable	Method of monitoring
1.	Calibration gas	Analyze calibration gases using Method 6 as part of routine operating procedures or as the need is indicated by other checks. See section 5.11.3.5 page 2-51.
2.	Zero drift	Make zero check and adjustment as part of daily operating procedure. See section 5.11.3.7 page 2-69.
3.	Span drift	Make span check and adjustment as part of daily operating procedure and plot on control chart. See section 5.11.3.7 page 2-69.
4.	Response time	Check response time as part of bi-weekly operating procedure. See section 5.11.3.7 page 2-69.
5.	Dynamic calibration	Perform a dynamic three-point calibration as part of bi-weekly operation procedure or as needed due to major system modifications. See section 5.11.3.7 page 2-69.
6.	Replicate sampling (audit)	Manually sample the stack gas, analyze the sample, and determine a sulfur dioxide concentration as directed by the appropriate reference method. See section 5.11.4 page 2-75.
7.	Data processing check	Manually check a randomly chosen week of data for proper use of calibration data, reasonableness of the averaged data, and correct transfer functions. See section 5.11.4 page 2-75.

3. The use of $\overline{X}$ (mean) or $\overline{R}$ (range) or other control charts and tests for significance of differences to gain more information about troublesome or out-of-control tests or methods.

Figure 5.11.1 illustrates in a block diagram the method procedural relationships for Performance Specification 2 as applies to the measurement of sulfur dioxide.

5.11.2 Plan Activity Matrix

5.11.2.1 Purpose--Quality control procedures and checks are designed to identify invalid data and to assure that the reported data are of acceptable quality. These procedures and checks should be integral parts of the normal operational functions. Special quality control checks or procedures may be required of the field operator if deemed necessary by the supervisor in charge of the field operations. The need for such exercises would be a function of the type of source and the adequacy of the monitoring system.

Instructions for the continuous measurement of sulfur dioxide are directed primarily toward 2-week performance tests during which the compliance of the monitored source is determined. The continuous data generated from the monitoring system other than during the performance test period provide a daily indication of the operation and maintenance of the process and emission control equipment. An auditing level of one audit check every six months and three audits per performance test period is recommended in this document. All apparatus should satisfy Performance Specification 2 (section 5.11.1), and manufacturer's recommendations should be followed whenever possible.

This section presents, in tabular matrix form, a synopsis of control procedures for important sources of variation

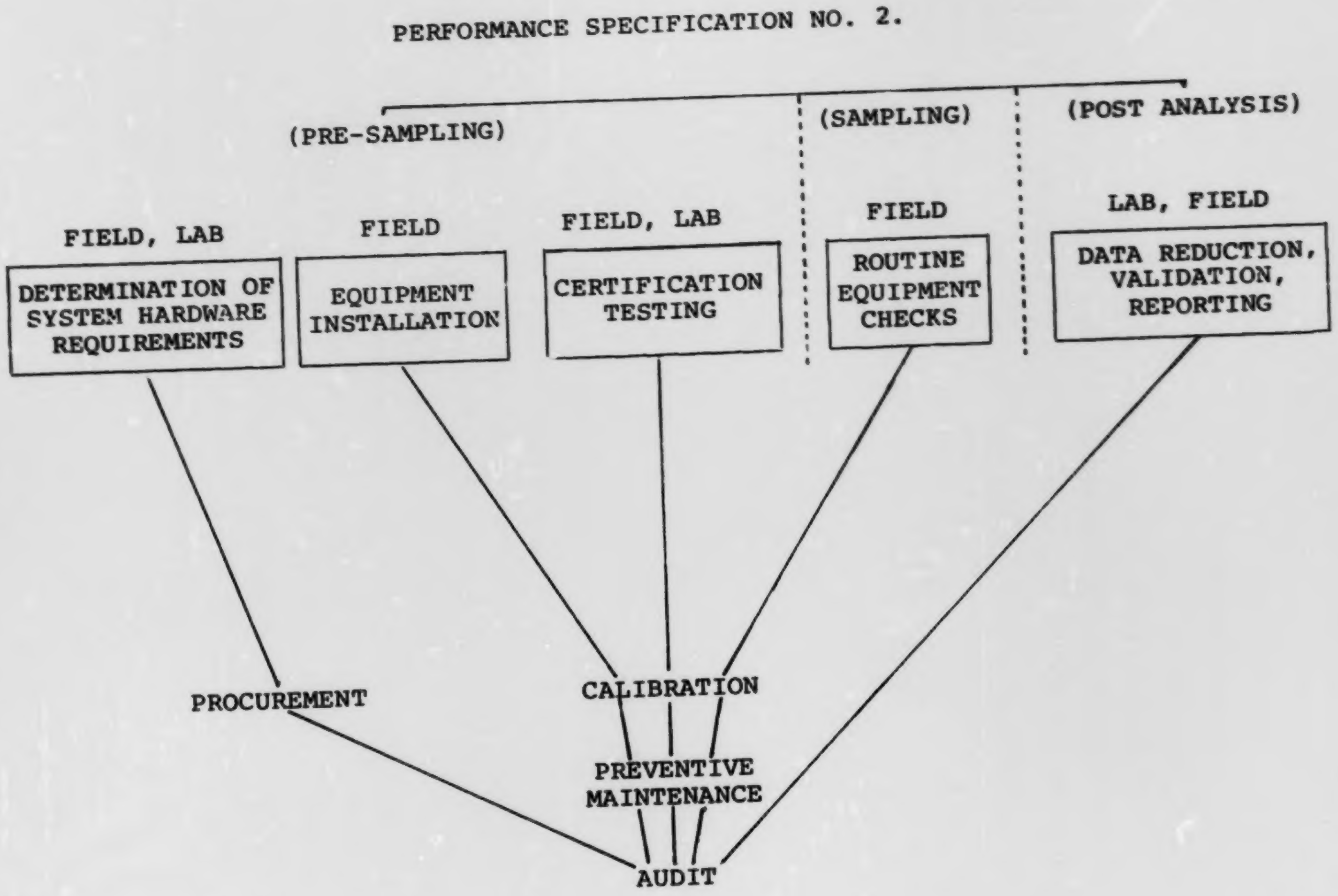

PERFORMANCE SPECIFICATION NO. 2.
(PRE-SAMPLING)
(SAMPLING)
(POST ANALYSIS)
FIELD, LAB
DETERMINATION OF SYSTEM HARDWARE REQUIREMENTS
FIELD
EQUIPMENT INSTALLATION
FIELD, LAB
CERTIFICATION TESTING
FIELD
ROUTINE EQUIPMENT CHECKS
LAB, FIELD
DATA REDUCTION, VALIDATION, REPORTING
PROCUREMENT
CALIBRATION
PREVENTIVE MAINTENANCE
AUDIT

Figure 5.11.1 Method procedures relationships.

associated with the operating procedures. Each important measurement or control procedure is identified in a block at the left of the tabular matrix. The information in the blocks across the page indicates for each procedure: the acceptance limits, the frequency of the check or measurement, the action to be taken if requirements are not met, and the disposition of records. Stepwise instructions for performing each operation in the matrix appear in the corresponding subsection of section 5.11.3, "Operation Procedures," or, in the case of audit instructions, in section 5.11.4, "Auditing Procedures."

The operational categories have been subdivided into the following operational areas, which more readily lend themselves to a tabular formation:

5.11.2.2 System Definition and Procurement
5.11.2.3 Installation and Instrument Check
5.11.2.4 Performance Testing
5.11.2.5 Data Reduction, Validation, and Reporting
5.11.2.6 Operating Procedures for Non-Compliance Monitoring
5.11.2.7 Auditing Procedures.

PLAN ACTIVITY MATRIX

5.11.2.2 System Definition and Procurement

Characteristic	Acceptance Limits	Frequency of Check or Measurements	Method of Measurement	Action If Requirements Not Met	Record of Check
Analyzer**	Manufacturer's specifications must meet requirements outlined in section 5.11.1.4	Upon purchase of instrument	See section 5.11.3.3.7	Reject or modify instrument as required	Equipment logbook
Sampling interface **	Must condition the sample to the stage where it is compatible with the analyzer	Prior to installation in the field and actual assembly with analyzer	Simulate a typical sample input and measure the appropriate parameters at the output of sample interface	Reject or modify the sampling interface	Equipment logbook
Calibration gas mixtures-sulfur dioxide in oxygen-free nitrogen or air**	Average of measured concentration values within 5 percent of stated values	Upon receipt of mixtures	Analyze by Method 6 See section 5.11.3.3.7	Reject gas mixture	Equipment logbook
Zero gas*	Must contain less than 1 ppm SO_2	Upon receipt of mixture	Pararosaniline Method	Reject gas mixture	Equipment logbook
Method 6 equipment*	Must meet specifications stated in ref. 1	Prior to test	As directed in ref. 1	Modify or repair system as necessary	Equipment logbook
Method 8 equipment (as applicable)*	Must meet specifications stated in ref. 2	Prior to each test	As directed in ref. 2	Modify or repair system as necessary	Equipment logbook
Chart recorder*	Must meet specifications stated by manufacturer	Upon purchase	See section 5.11.3.3.7	Reject recorder	Equipment logbook

** Indicate a critical check; i.e., one which must be controlled within the specified tolerance in order to obtain acceptable data.

* Indicates a noncritical check; i.e., one which allows small out-of-tolerance variations without significantly affecting data quality

PLAN MATRIX ACTIVITY

5.11.2.3 Installation and Instrument Check

Characteristic	Acceptance Limits	Frequency of Check or Measurements	Method of Measurement	Action If Requirements Not Met	Record of Check
Sampling interface system**†	1. Absence of moisture and foreign materials in any traps 2. Absence of breakage, loose connections, or foreign materials in tubing 3. Absence of air leaks in sample line and cooling lines (if used) 4. Proper operation of heating and cooling systems	Once per week or whenever monitoring system is shut off and sampling is to begin again	Visual check	Clean or repair system components as required	Operational data logbook
Zero and span calibration**	1. Zero adjustment must be ≤ 5 percent of full scale	After a sufficient warm-up period upon start-up of the system and twice per day during normal operation	Determine from strip chart readings (section 5.11.3.5.2)	Perform dynamic calibration (applicable to extractive monitors only)	Operational data logbook
Analog chart recorder*	1. Absence of malfunctions 2. Adequate ink supply 3. Recorder time agreement with clock time 4. Dead band	Upon start-up of the system and once per day thereafter	Visual	Repair recording system	Operational data logbook
Magnetic tape recording system (if used)*		Once per week	Visual review of printed listing of raw data	Reduce data as soon as possible and repair recorder as suggested by manufacturer	Operational data logbook

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†If applicable to the system being installed.

PLAN MATRIX ACTIVITY

5.11.2.4 Performance Testing

Characteristic	Acceptance Limits	Frequency of Check or Measurements	Method of Measurement	Action if Requirements Not Met	Record of Check
Calibration gas mixtures**†	≤ 5 percent change from calculated average from last check	At performance test and once every 6 months	Take three samples of each mixture and, using Method 6, determine average concentration of each mixture	Reject calibration mixture	Operational data logbook
Calibration error**	≤ 5 percent of each calibration gas mixture value or if the range of readings ≤ 10 percent of cylinder concentration	At performance test and once per week during normal operation	Manufacturer's instruction. See section 5.11.1.5	Recalibrate system	Operational data logbook
Zero drift*	1. (2 hour) ≤ 2 percent of span 2. (24 hour) ≤ 2 percent of span	Make 15 2-hour interval determinations and 7 24-hour determinations	See section 5.11.3.5.2	Identify cause of drift, take corrective action, and recalibrate	Operational data logbook
Calibration drift**	1. (2 hour) ≤ 2 percent of span 2. (24 hour) ≤ 5 percent of span	Make 15 2-hour interval determinations and 7 24-hour determinations	Calculate from span drift and zero drift data See section 5.11.3.5.2	Identify cause of drift, take corrective action, and recalibrate	Operational data logbook
Accuracy**	≤ 20 percent of mean value of the reference method test data	Test for accuracy for one week during each performance test	Compare to Reference Method results as described in section 5.11.1.5.	Reject analyzer or repair, replace, or clean component parts as required	Operational data logbook
Response time*	15 minutes maximum	Three times during performance testing	As described in section 5.11.1.5	Reject analyzer or repair, replace, or clean components which are malfunctioning	Operational data logbook

†When applicable to system being installed.

PLAN MATRIX ACTIVITY

5.11.2.5 Data Reduction, Validation, and Reporting

Characteristic	Acceptance Limits	Frequency of Check or Measurements	Method of Measurement	Action if Requirements Not Met	Record of Check
Stripchart evaluation*	Absence of evidence in the stripchart trace of system malfunction	Once per day	Visual check	Determine cause of malfunction and take corrective action immediately	Operational data logbook
Data reduction requirements	One hour averages shall be computed from four or more data points equally spaced over each 60 minute period commencing on the hour	Upon change of chart paper	Visual check and stripchart reading	Void intervals identified as invalid during monitoring period	Data record
Data reporting	Data must be properly logged with all calibration and accuracy data included with the data	Following data reduction from stripchart	Visual check	Obtain missing data from record files or determine reasons for missing information	Data analysis reports
Control charts	Daily recording of zero and span check adjustments	Daily	Visual check	Obtain data from system operator and add to control chart data	Data analysis reports

PLAN MATRIX ACTIVITY

5.11.2.6 Operational Procedures for Non-Compliance Monitoring

Characteristic	Acceptance Limits	Frequency of Check or Measurements	Method of Measurement	Action if Requirements Not Met	Record of Check
Dynamic calibration**	Maximum deviation of 5 percent from regression curve	Once every 2 weeks	See section 5.11.3.5.1	Prepare a new calibration curve	Operational data logbook
Zero and span calibration**	≤ 5 percent change from last adjustment with no more than four consecutive changes with the same sign	Once per day	See section 5.11.3.5.1	Perform dynamic calibration	Operational data logbook
Accuracy**	≤ 20 percent of reference mean value	Once every 3 months or whenever a major change is made in sampling interface or the analyzer. Once per month if the entire system is not dynamically calibrated every 2 weeks	As described in section 5.11.1.5 except make only three Method 8 measurements	Make necessary modifications or repairs on system and repeat performance test	Operational data logbook
Recording system*	1. Absence of malfunction 2. Adequate ink supply 3. Correct recorder time 4. Wear on mechanical parts 5. Proper lubrication	Once per day or as indicated by experience with recorder in use	Manufacturer's instructions	Repair or replace as necessary	Operational data logbook
Sampling interface**	Absence of malfunctions, leaks, etc.	Once per week	Manufacturer's instructions	Repair or replace components as necessary	Operational data logbook

PLAN MATRIX ACTIVITY

5.11.2.7 Auditing Procedures

Characteristic	Acceptance Limits	Frequency of Check or Measurements	Method of Measurement	Action if Requirements Not Met	Record of Check
Sampling probe, interface, and analyzer system inspection	Proper operation and cleanliness of all components	Once per performance test and at least once every 6 months during non-compliance monitoring	Visual	Report discrepancies to supervisor for rectification. Increase frequency of audits until results of visual inspections improve to a satisfactory level	Audit logbook
Reference method sample extraction and analysis	1. Sampling point must be adjacent to continuous system's sampling point 2. Accuracy calculated based on Reference Method data and corresponding continuous system data shall not exceed 20 percent of reference mean value (section 5.11.1.4)	A minimum of four Method 6 or Method 8 measurements per performance test and a minimum of four every 6 months during non-compliance monitoring	Section 5.11.4.2	Reason for inaccuracies must be determined and the audit rate increased until audit results indicate that the data quality has reached a satisfactory level	Audit logbook
Reference samples	Results of analysis must be within ±20 percent of the predetermined calibration gas mixture value and the average difference of results should not exceed 10 percent of calibration gas mixture value	Once every six months in lieu of reference method sampling discussed above	Section 5.11.4.2	Corrective action and repeat measurements with reference samples	Audit logbook

PLAN MATRIX ACTIVITY

5.11.2.7 Auditing Procedures (cont.)

Characteristic	Acceptance Limits	Frequency of Check or Measurements	Method of Measurement	Action if Requirements Not Met	Record of Check
Data processing	Original results must be within: 1. ± 3 percent of audit data for stripchart recording systems, or 2. ± 1 percent of audit data for magnetic tape recording system	Once per performance test and one week per 6 months of non-compliance monitoring	Manual calculations beginning with raw data (section 5.11.4.3)	Increase frequency of audit until problem is eliminated or minimized	Audit logbook

5.11.3 Operational Procedures

5.11.3.1 General Considerations--In the subsections immediately following, specific procedures for measuring and reporting sulfur dioxide emissions from stationary sources using continuous monitors are described. The sequence of operations to be performed is given in figure 5.11.2. Two sets of columns are used. The left-hand set, with items numbered 1 through 24, lists operating procedures in sequential order for a given monitoring system. Calibration, maintenance, and procurement procedures which are performed periodically are listed A through F in the right-hand set of columns. Quality checkpoints in the measurement process for which appropriate quality control limits are assigned are represented by blocks enclosed by heavy lines. Other checkpoints involve subjective judgments by the operator with proper guidance as indicated in the procedures.

Directions throughout this manual are written in terms of two modes: first, the performance testing mode, and secondly, the continuous operation mode. Audit or checking levels of three checks per 1-week operational test period and one check every six months during non-compliance continuous operation are assumed.

Examples of various pages which might be included in operational records are given throughout this manual. The operational records should include:

1. Operational Data Logbook
2. Sampling Recorder Stripchart
3. Hourly Averages Record Sheet
4. Calibration Logbook
5. Equipment Logbook
6. Maintenance Logbook
7. Performance Testing Logbook
8. Audit Logbook

Sequence of Operations

1. Study the type of source, physical parameters, and existing sampling media
2. Research and define system compatible with results of above study
3. Procure defined system including interface equipment, analyzer, and recording apparatus
4. Install entire system per manufacturer's instructions and section 5.11.1.4
5. Use Method 6 procedures to analyze calibration gases

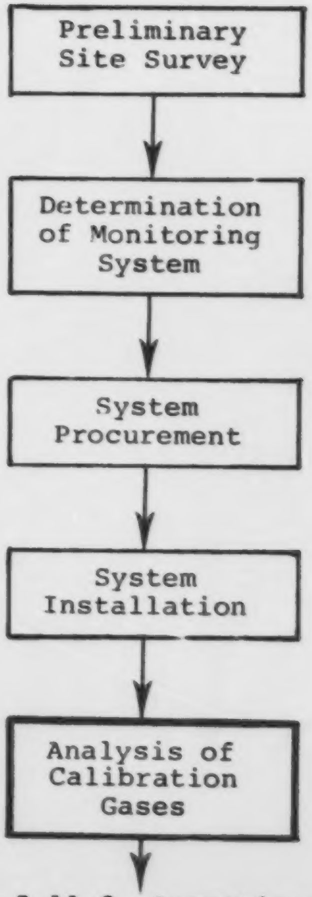

Preliminary Site Survey
Determination of Monitoring System
System Procurement
System Installation
Analysis of Calibration Gases

Figure 5.11.2 Operational flow chart

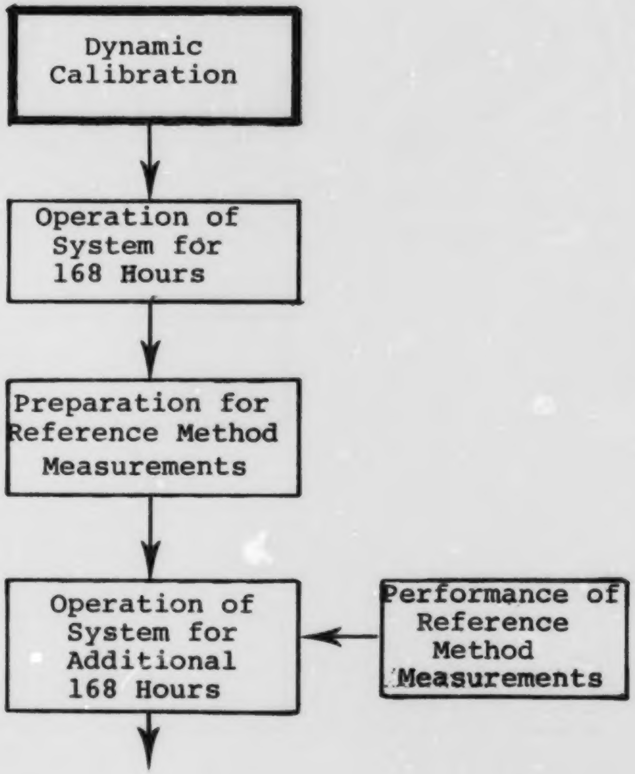
Sequence of Operations

6. Perform calibration at 0, 50, and 90 percent of span

7. Operate system normally per manufacturer's instructions

8. Prepare reagents and install sampling train for Reference Method measurements

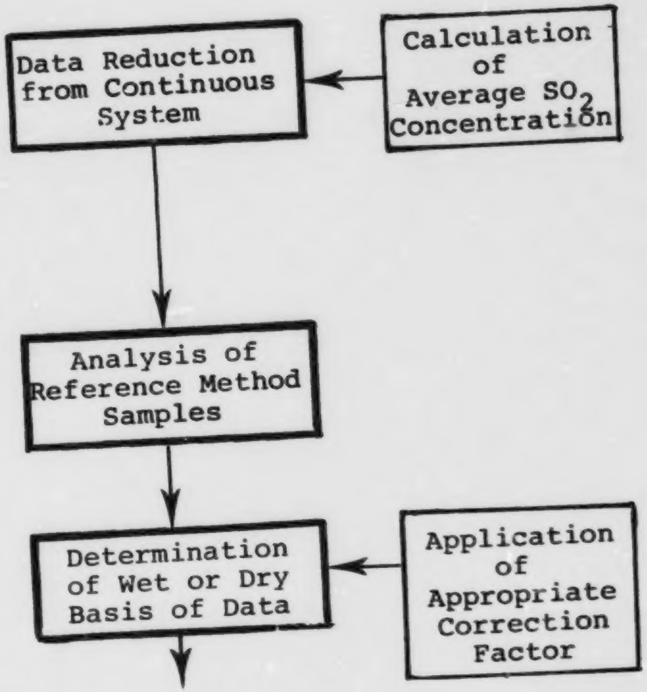
9. Monitor source effluent continuously


Dynamic Calibration
Operation of System for 168 Hours
Preparation for Reference Method Measurements
Operation of System for Additional 168 Hours
Performance of Reference Method Measurements

A. Make a minimum of nine SO_2 concentration measurements during 168-hour test period

Figure 5.11.2 (cont.) Operational flow chart

Sequence of Operations


Data Reduction from Continuous System
Calculation of Average SO_2 Concentration
Analysis of Reference Method Samples
Determination of Wet or Dry Basis of Data
Application of Appropriate Correction Factor

10. Tabulate 15-minute data read from stripchart or magnetic tape recording system

B. Manually or with computer, calculate average SO_2 concentrations for the time intervals coincident with nine Reference Method sampling periods

11. Following appropriate Reference Method procedures, analyze samples and calculate SO_2 concentrations

12. The basis for Reference Method data and continuous data must be consistent to compare data

C. Determine correction factor after measuring moisture content of the stack gas per revised Reference Method 4 procedures

Figure 5.11.2 (cont.) Operational flow chart

Sequence of Operations

13. Subtract Reference Method concentration from continuous value for each of the nine intervals

14. Compute the mean of the nine differences and report

15. Compute and report the upper limit of the 95 percent confidence interval

16. Calculate and report the accuracy as a percentage of the mean reference value

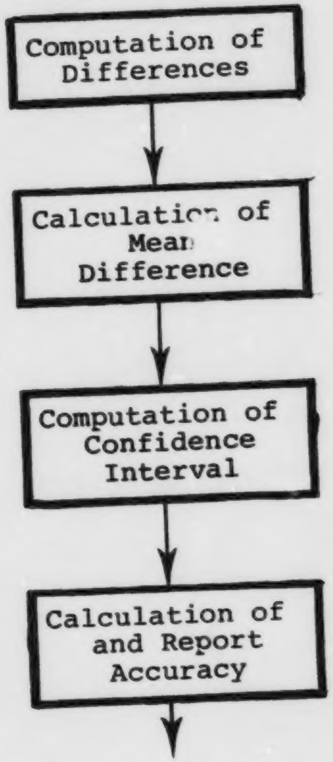
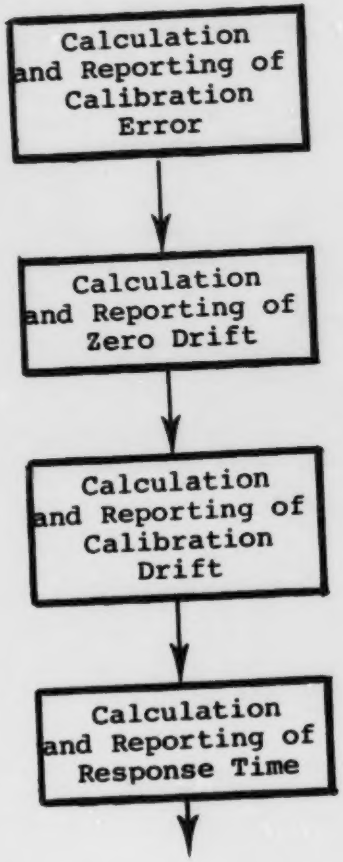

Computation of Differences
Calculation of Mean Difference
Computation of Confidence Interval
Calculation of and Report Accuracy

Figure 5.11.2 (Cont.) Operational flow chart

Sequence of Operations


Calculation and Reporting of Calibration Error
Calculation and Reporting of Zero Drift
Calculation and Reporting of Calibration Drift
Calculation and Reporting of Response Time

17. Compute difference between actual and resulting calibration values and calculate error

18. Calculate and report 2-hour and 24-hour zero drift as percentage of span

19. Calculate and report 2-hour and 24-hour calibration drift as percentage of span

20. Calculate response time for all upscale and downscale tests, the mean values, and report the slower time

Figure 5.11.2 (Cont.) Operational flow chart

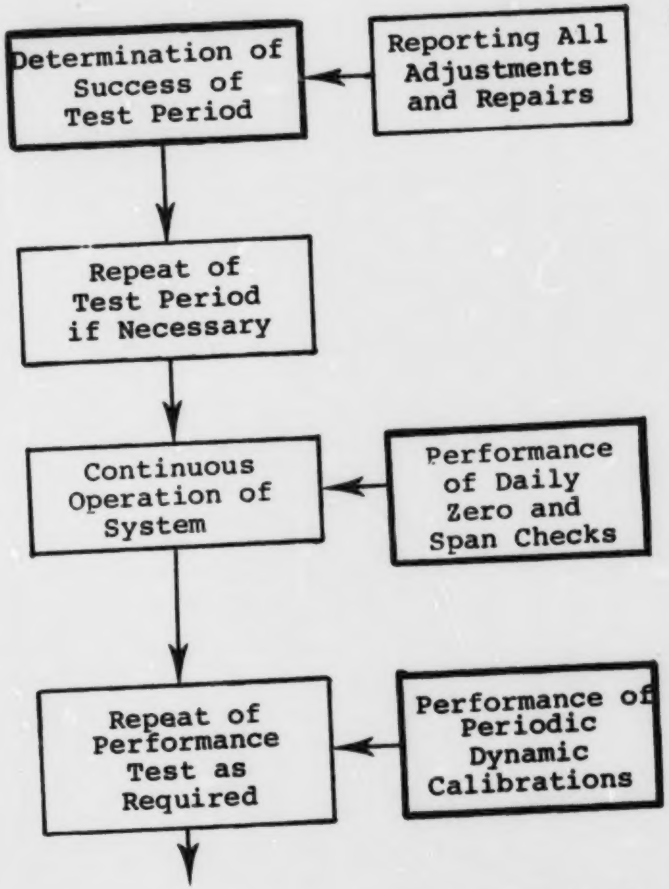
Sequence of Operations

21. If the Performance Specifications in section 5.11.1 are met and no corrective maintenance, etc. was required during test period, test was a success

22. Repeat performance testing if original test was not a success

23. System should monitor the stack effluent and record the data continuously

24. Repeat performance test as required for compliance data ·


Determination of Success of Test Period
Reporting All Adjustments and Repairs
Repeat of Test Period if Necessary
Continuous Operation of System
Performance of Daily Zero and Span Checks
Repeat of Performance Test as Required
Performance of Periodic Dynamic Calibrations

D. Any corrective maintenance or adjustment must be logged

E. Automatic and/or manual zero and span checks should be performed daily and adjustments should be logged

F. Dynamic calibrations should be performed bi-weekly or after any corrective maintenance

Figure 5.11.2 (Cont.) Operational flow chart

5.11.3.2 Preliminary Site Study--The optimum continuous monitoring system for sulfur dioxide in stack gases can only be defined after an in-depth study of the source in question has been accomplished. The more important parameters which will influence the choice of a system include:

1. Moisture content of the stack gas;
2. Stack gas temperature, temperature fluctuations, stack gas velocity, and static pressure;
3. Existence of other gaseous components in the stack gas, e.g., oxides of nitrogen, sulfuric acid;
4. Possible physical location of the sampling system, an optimum sampling point, and physical dimensions of the stack;
5. Particulate loading evident in the effluent;
6. Range of sulfur dioxide emission rates;
7. Ambient temperature range;
8. Level of competence and experience of the personnel who will be charged with the operation and maintenance of the monitoring system; and
9. Availability of laboratory facilities.

Most of the information asked for in the above list can be obtained in a single visit to the plant site if not attainable from previously accumulated data from the same or similar plants. Portable instrumentation is available to measure some of the stack gas characteristics, i.e., pressure gage and dial thermometer. The moisture content measurement can be made using Method 4, Determination of Moisture Content in Stack Gases (ref. 3). The gaseous constituents of the stack gas can be determined with an Orsat analysis or estimated from details of the particular process in question. The other parameters can be sufficiently covered in discussions with the plant operator(s).

5.11.3.3 System Definition and Procurement--The determination of the optimal monitoring system for a given stack must be made only after the preliminary site survey and a careful study of several other parameters have been executed. These parameters include:

1. Overall objective of the monitoring system program,
2. Expected operation and maintenance requirements which can be tolerated by the program,
3. Need for ease in calibration,
4. Auditing program requirements which may be enforced.

In defining the overall objective of the sampling system, the simplicity or complexity desired in the monitoring system should become evident. The second parameter is definitely dependent on parameter number 8 in section 5.11.3.2, the level of competence and experience of the personnel to be charged with the operation and maintenance of the system. Along these lines, too, is the number of hours per week or per month of the personnel's time which will be alloted to this role. The need for ease in calibration will also be a function of the operator's time and skills. As a result of defining potential audit requirements, only systems with the desired characteristics for auditing (i.e., reference gas inlets, etc.) will be considered.

As stated in section 5.11.1.2 the system apparatus will consist, generally speaking, of equipment for the reference method measurement of the sulfur dioxide concentration, calibration media, a continuous monitoring system (several varieties of which are discussed below), and a data recorder. The data recorder can be either an analog chart recorder or any other suitable device with an input voltage range compatible with the output of the analyzer system. If a magnetic tape recording system is selected, a backup strip chart recorder is recommended to meet immediate operation, maintenance, and troubleshooting needs.

Several types of continuous sulfur dioxide monitoring systems are commercially available utilizing a wide range of detection techniques. There are two main classifications for these systems: in-situ and extractive. The in-situ measurement system has the monitor mounted directly on the stack where it senses the pollutant in the effluent stream without need for removing samples from the stack gas. The majority of the in-situ monitors are based on optical methods for taking the measurement at a point in the stack or taking a spatially integrated measurement across the diameter of the stack. The extractive monitor is one which requires the sample to be drawn from the stack and transported to the analyzer. Depending upon the distance from the sampling point to the analyzer and the analyzer's sample conditioning requirements, the interface between the sampling point and the analyzer can vary in complexity. Several in-situ and extractive monitors are discussed below with indications given as to the types of interfaces which might be considered when appropriate.

5.11.3.3.1 Dispersive spectroscopy. Several instruments are available which utilize dispersive spectroscopy to measure the gases across the stack rather than drawing a sample out of the stack. One such instrument transmits a beam of light from one side of the stack to the other so that it passes through the gas stream. The polychromatic light beam contains certain wavelengths of light which are optically absorbed by various constituents of the gas. Hence, the reduction in the intensity of the beam at a given wavelength as it is received at the opposite side of the stack is proportional to the number of molecules of the constituent absorbing at that wavelength. The analyzer section of the instrument isolates the wavelengths of interest (for SO_2 the corresponding wavelength is 3024 Å) and measures their individual intensities.

A monitoring system of this type, although theoretically simple, must be designed to withstand and/or compensate for changes in ambient temperature and severe vibrations which are likely at various times of the year. Other practical problems which must be overcome include:

1. Calibration of the entire system.
2. Keeping the windows which separate the analyzer and the stack gas clean,
3. Particulate concentrations in the stack gas which will reduce transmission of the subject wavelength by blocking its path rather than by SO_2 absorption,
4. Maintaining constant intensity of the source lamps,
5. Guaranteeing that the detectors maintain the same detection sensitivity.

Two common variations to the dispersive spectroscopy "double-ended" instrumentation described above are the "folded path" design and the "slotted pipe" design. Unlike the "double ended" system, the "folded path" system places both the source and receiver at the same location. The energy beam is transmitted through a slotted probe and reflected back into the instrument for analysis. The "slotted pipe" extends either between the transmitter and receiver or between the transmitter/receiver combination and the reflector. The purpose of the slotted pipe is either to prevent misalignment or to restrict the absorption pathlength to maintain linear detector response.

One example of the more sophisticated "folded path"/"slotted pipe" instruments is one which utilizes a flat zero/read mirror. When the mirror is in the read position, reflected light is directed back to the spectrometer. If SO_2 is present in the slotted pipe, it will absorb energy in regularly spaced bands of 3024 Å. The light reflected off the mirror is reflected onto a diffraction grating which disperses the light allowing for a spatial display of the absorption spectra of SO_2. When the mirror is in the calibration position, the light is directed into the spectrometer bypassing the sample probe which serves as a zero check. A temperature-stabilized gas cell containing a known concentration of SO_2 can then be inserted into this same path to provide a span check.

An alternative to changing the position of the mirror is to utilize a second light source in the analyzer which does not pass through the stack gas. By inserting either a gas cell of known concentration or a calibrated optical filter in the path of the second beam, a calibration can be performed.

A possible means of performing a dynamic calibration is to insert standard verified sealed cells into the path of the original beam which will incrementally add to the unknown stack gas. In this way a system operating curve can be determined. The entire dynamic calibration procedure can be accomplished automatically using a timer actuated solenoid arm (ref. 5). Care must be taken, however, that the certification value for the cell is determined at temperatures equivalent to existing stack gas conditions. An alternative is for the manufacturer to supply a calibration curve and to apply the appropriate correction factors at each calibration.

Another of the problems stated above which has been examined by several manufacturers is that caused by the accumulation of particles on the windows which would block transmission of the light beam. A system designed to alleviate this problem is one which uses a specially designed forced-air purge system to avoid dirt buildup on the windows and adjoining hardware. The air for the system is supplied by a self-contained blower which works continually (ref. 6).

The third problem stated above deals with the particulate loading characteristic of the stack gas. A relatively simple way to avoid this problem is simultaneous detection of two wavelengths of the polychromatic light beam in a double-ended system or of the reflected light in the folded path system. One wavelength, of course, is that which is absorbed by SO_2. The second is a reference wavelength not absorbed by any stack gas constituent. Any deterioration of the intensity at the second wavelength is not due to absorption and must be caused by interference from the particulates in the gas stream. This deterioration at the second wavelength can be appropriately assigned to the first wavelength as an addition to the originally measured intensity.

5.11.3.3.2 Second derivative spectroscopy. Second derivative spectroscopy is another in-situ method for measuring SO_2 in stack gas emissions. It is an attempt toward greater specificity and resolution by determining the derivatives of the intensity with respect to wavelength of a light beam which has passed through the stack gas. The optical technique used in this type of instrument is wavelength modulation where the wavelength radiation is modulated sinusoidally with time.

One instrument utilizing this technique has within it a grating monochrometer which spectrally disperses the radiation from an ultraviolet source. The wavelength of this monochromatic radiation is then varied with respect to time by laterally oscillating the entrance slit position electromechanically at a frequency of 45 hertz. The amplitude of the wavelength modulation can vary depending on the peak-to-peak displacement chosen between .25 and 1 mm. The signal then enters an absorption cell with a wavelength centered about a value set by the grating position and slightly modulated in time at 45 hertz.

In the absorption cell, the light is reflected back and forth across the length of the cell several times until it is focused on a detector which is generally a photomultiplier tube. The 90 hertz component of the output signal from the photomultiplier tube is electronically analyzed using a fundamental phase-lock amplifier technique. The amplitude of the 90 hertz signal is presented as an output dc voltage which is proportional to the second derivative of intensity with respect to wavelength. Electronically dividing this signal by the total output voltage of the PM tube results in a signal proportional to gas concentration (ref. 7).

All of the problems stated in section 5.8.3.3.1 are applicable to the second derivative spectroscopy method. Calibration at selected concentrations can be made manually or automatically using standard, sealed samples of SO_2 which are inserted into the light path internally to provide measurements corresponding to known concentrations. The problem of accumulation of particulates on the windows encasing the optics can be handled in very much the same way as stated above. Because the technique is sensitive to particulates in the stack gas, a ceramic probe filter can be used so as not to allow particulates to enter into the measurement. All of the electronics are located separately from the optics which are in a sealed encasement. With this situation then, preventive maintenance on the electronic components can be performed without disturbing the rest of the system.

Two other parameters which should be discussed in relation to second derivative spectroscopy are: sensitivity to high stack gas temperatures and interferences by other constituents of the stack gas. Designs available on the market today can withstand stack gas temperatures up to 540°C. Some specificity can be lost in the ultraviolet absorption method when two different constituents have absorbed some amount of energy at a given wavelength. In other words, at wavelength λ_o, several constituents may add to the reduction in intensity. However, with this technique of optically determining the second derivative, the amount of loss of intensity due to SO_2 can readily be differentiated from absorption by any other constituent.

5.11.3.3.3 Extractive ultraviolet absorption. One of the more simple extractive methods is that which extracts a sample of the stack gas, maintains the sample at the high stack gas temperatures, analyzes the sample for the sulfur dioxide content, and then discharges the sample back into the flue gas. Either a split beam or a dual beam source can be used in the analysis. Simply, the first beam, at a given wavelength absorbed strongly by SO_2, passes through the sample cell through which the sample of stack gases flows. The intensity of the light is detected by a wavelength phototube along with the intensity of a second beam. The second beam has passed through an optical filter that transmits only the reference wavelength which is not absorbed by sulfur dioxide and then through the sample cell simultaneously with the first beam. The phototubes generate electrical signals which are proportional to the intensity of each signal. The logarithms of the two signals can then be compared and a single photometer signal outputted which is proportional to the concentration.

Advantages of such a system include:

1. Long sample lines are not required when the photometric system is mounted on the stack;
2. Systematic errors such as particulate buildup on the windows of the sample cell are avoided because of the use of a reference;

3. System components are at a minimum so that troubleshooting and the subsequent repair of equipment should require considerably less time than other more sophisticated systems;
4. Response is generally linear over a wide range;
5. The optics, the electronics, and the sample cell can be isolated from each other which allows the operator to perform maintenance on any one of the three without affecting the others;
6. Zero calibration can be performed by simply backflushing the probe and sample cell which simulates zero absorption;
7. Span calibration can be performed by dropping a reference cell of known concentration into the path of the light beam during the backflushing operation;
8. Due to the elevated temperatures of the sample at all times, problems due to condensation and corrosion of equipment may be avoided;
9. An air aspirator is used to extract the sample as opposed to a sample pump which is generally much less reliable for long-term monitoring;
10. A system such as this can be readily adapted to several different sources (ref. 8).

5.11.3.3.4 Nondispersive infrared. Most analyzers using the nondispersive infrared (NDIR) technique consist of either one light source with a light chopper or two identical sources whose beams are directed through two different cells. One of the cells contains a gas which does not absorb infrared energy at the same wavelengths at which sulfur dioxide absorbs infrared energy. Passing through the other cell is the sampled stack gas. The beams pass through both of these cells and into different half sections of a reference chamber. Separating the two half sections of the reference chamber is a flexible metal diaphragm. Both sections contain the same amount of SO_2 vapor kept at the same atmospheric pressure. The degree of absorption of infrared energy by the sample gas is directly proportional to the amount of SO_2 in the sample gas. The absorption by the sample gas will proportionally reduce the absorption by the SO_2 vapor in the corresponding half section of the reference chamber. The difference between the energy absorptions in the two halves on the reference chamber, then, is a measurement of the concentration of SO_2 in the sample gas.

The flexible metal diaphragm when used with a stationary metal plate forms one side of two-plate variable capacitor. The capacitance, which changes with the detention of the diaphragm, is measured. The detention of the diaphragm is proportional to the difference between the energy absorption of the SO_2 vapor in the two sides of the reference chamber. Hence, an electrical signal is generated which is proportional to the concentration of SO_2 in the sampled stack gas.

The primary sources of error in the NDIR method are the blocking of the transmission of the light beam by particulates and the inadvertent absorption of infrared energy by moisture in the sample gas. Both of these sources of error can be minimized by adequate interfacing equipment, varieties of which will be discussed below.

The sampling interface used with an NDIR analyzer must be capable of removing fly ash and particulate matter as well as removing or determining the quantity of moisture in the sample. Particulate matter will tend to collect on the windows of the sample cell. Water vapor will interfere inasmuch as the SO_2 absorption band is overlapped by a water system in the $1200\ cm^{-1}$ to $1400\ cm^{-1}$ region.

One possible sampling interface is described in reference 6 and shown in figure 5.11.3. The 0.5 micron filter used in this system is adequate for removal of the small amount of particulate in the emission from a source having a bag house in use. The filter is placed in the stack as a portion of the sample probe. Heat from the stack gas will keep the filter hot and keep moisture from condensing as the gas is drawn through the filter. When stack gases are not filtered by a bag house filter system or equivalent, it is necessary to install a portable bag house-type filter ahead of the 0.5 micron filter in the sample line.

The sample gas transmission line shown in figure 5.11.3 is made up of 100-foot long Teflon segments with an individual heating system for each segment. The overall transmission heating system should maintain a nominal 120°C (250°F) gas temperature from the sample probe to the first heat exhanger.

The heated gas from the transmission line is rapidly cooled from 120°C (250°F) to 1°C (34°F) to remove all moisture. To do this, a heat exchanger is usually employed to reduce the gas temperature between 55 and 85°C (100 to 150°F) depending on the atmospheric temperature. The sample gas is then passed through an electro-mechanical refrigeration unit to further reduce the gas temperature. Approximately 90 percent of the sample gas is then removed from the conditioning system via the stack gas pump. The remaining sample gas is passed through a second electro-mechanical refrigeration unit to reduce the gas temperature to approximately 1°C (34°F). The reduction of temperature causes the moisture in the gas to condense into a liquid. A collection device is employed in conjunction with the above conditioners to remove the liquid from the system and holds the liquid for later measurement as evidence of the moisture content of the stack gas.

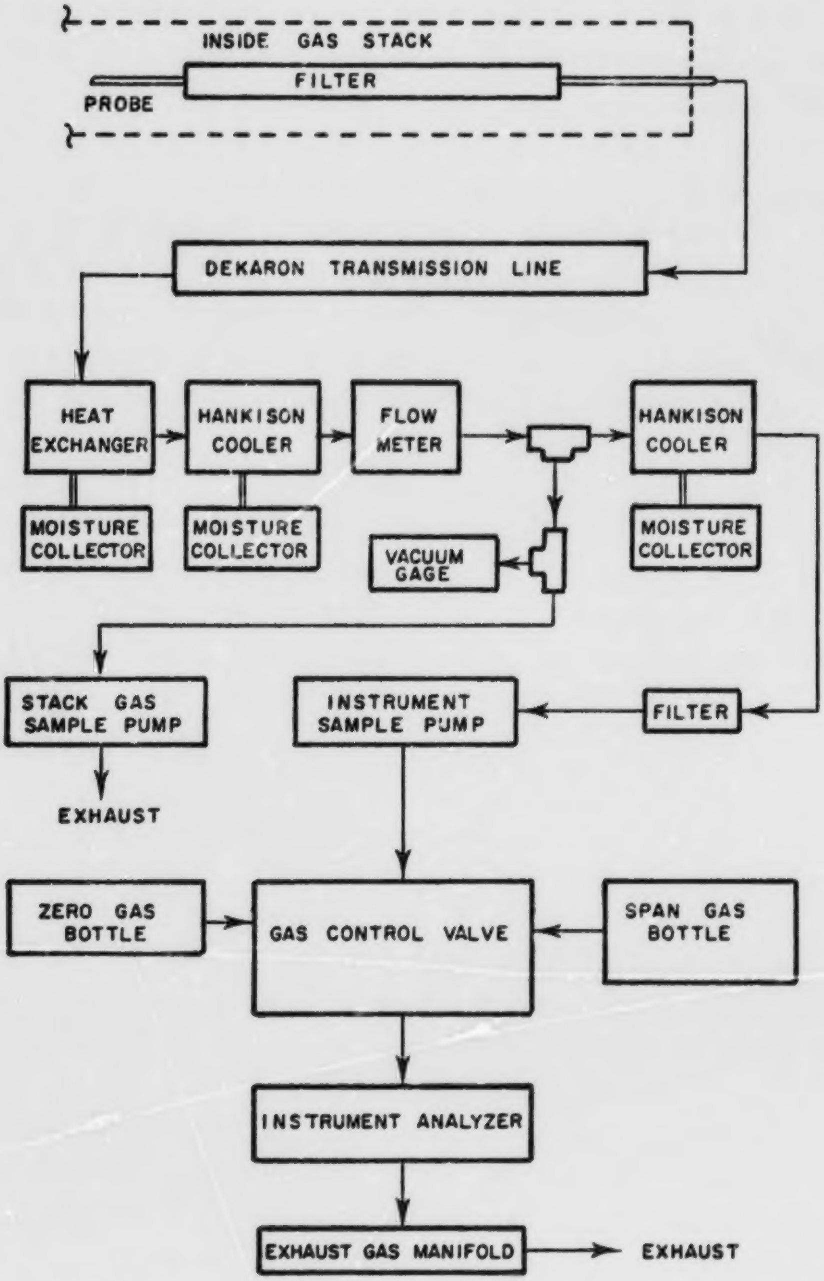

INSIDE GAS STACK
FILTER
PROBE
DEKARON TRANSMISSION LINE
HEAT EXCHANGER
HANKISON COOLER
FLOW METER
HANKISON COOLER
MOISTURE COLLECTOR
MOISTURE COLLECTOR
VACUUM GAGE
MOISTURE COLLECTOR
STACK GAS SAMPLE PUMP
INSTRUMENT SAMPLE PUMP
FILTER
EXHAUST
ZERO GAS BOTTLE
GAS CONTROL VALVE
SPAN GAS BOTTLE
INSTRUMENT ANALYZER
EXHAUST GAS MANIFOLD
EXHAUST

Figure 5.11.3. Example of an extractive sulfur dioxide monitoring system.

The stack sampling probe, when inserted in the stack, may be at either positive or negative pressure. A system for extracting the gas can either employ a pressure pump at the stack, which would require the pump to operate at high temperatures, or a vacuum pump located after the conditioning equipment. In the example illustrated in figure 5.11.3, the latter and more practical configuration is used. The sample gas leaving the pump is at a positive pressure sufficient to satisfy the flow rate and pressure needs of all analyzers. The pumped sample gas is then piped to the input of the gas analyzer.

5.11.3.3.5 Pulsed fluorescence. In the pulsed fluorescence method, the extracted stack gas sample is passed in front of a source of pulsed ultraviolet illumination equipped with a monochromatic filter. The molecules of sulfur dioxide contained in the sample will be energized by the high intensity light source and will emit a monochromatic illumination. This emitted light is linearly proportional to the concentration of sulfur dioxide molecules in the sample. It is usually sensed by a photomultiplier tube through a narrow-band filter and a proportional analog output is generated.

The most commonly used region of ultraviolet radiation is the 2300Å to 1900Å region. In this region sulfur dioxide molecules exhibit stronger absorption and their fluorescence is less likely to be quenched by other constituents of a stack gas (ref. 9).

The quenching effects of oxygen, carbon dioxide and nitrogen in concentration levels different from the ambient air levels are discussed in reference 10. Calibration of pulsed fluorescence analyzers is accomplished using SO_2-in-air reference mixtures which alters the analyzer accuracy for other constituent levels in the stack gas. As shown in test results discussed in reference 9, a reduction in oxygen level below 21% (ambient level) will linearly increase the analyzer reading. A rise in the CO_2 level in the stack gas will decrease the analyzer reading with respect to the true value. The quenching effects due to N_2 are negligible in comparison to effects due to O_2 and CO_2.

The level of water vapor content of the stack gas must be kept constant to avoid inconsistent quenching of the fluorescence. As discussed in reference 9, studies have shown that the pulsed fluorescent analyzer, which has included within its internal components a dryer which reduces the moisture to a very low and discernible level, will not require any external drying devices to maintain insensitivity to the moisture in the stack gas. In the case of pulse fluorescent analyzers without internal drying mechanisms, an external dryer or refrigeration unit must be used.

As in the majority of the extractive continuous analyzers, particulate removal is important so as not to clog the analyzer plumbing or to block the detection of light. Heated sample lines are also vital in preventing water condensation and the loss of sulfur dioxide from the sample.

Calibration of the system can be accomplished by inputting zero and span gases at the probe and/or at the analyzer.

5.11.3.3.6 Flame photometric detection. The flame photometric principle utilizes the detection of light, centered at 394 nm, emitted by sulfur-containing compounds when burned in a hydrogen-rich flame. The burning creates an excited state species of sulfur and the release of light energy upon the return to ground state sulfur is the quantity measurable with a photomultiplier tube optically shielded from the flame. The response of the detector, which generally views the light through a narrow band-pass interference filter, is directly related to the concentration of total sulfur entering the detector per unit time.

The advantages of a flame photometric detection system include: a high degree of sensitivity to sulfur compounds, low maintenance and downtime, and the fact that the system is readily calibrated using NBS traceable permeation tubes (ref.11). Disadvantages include downtime due to "flame-out," excessive analyzer drift, and sensitivity to small variations in gas pressures and flows. In addition, the analyzers available on the market for source monitoring purposes must be coupled with interface systems which have heated sample lines, remove particulates, dry the sample, and dilute the sample to within the measurement range of the air quality analyzer. The interface systems should also be equipped to remove all sulfur-containing compounds other than SO_2.

Several of the disadvantages listed above are taken care of in standard monitoring packages. Ceramic filters installed in the probe will remove the majority of the particulates and portable bag-house type filters can be installed downstream from the probe if more protection is necessary. Downtime form "flame-out" can be minimized with the use of an automatic flame reignition system which senses the flameout condition and corrects it by turning off or averting the hydrogen flow and reigniting the flame within 15 to 20 seconds. The hydrogen is then started up or redirected across the flame. The problem of drift can be avoided with daily or twice-daily calibrations. Utilizing an automatic calibration system is the most feasible way to meet this requirement.

There are several different types of dilution systems available. The disadvantages of all of them are:

1. The depletion of moisture is not adequate for most analyzers which have a characteristic sensitivity to water vapor.

2. A more complex gas control system is required to keep the flow rates constant.

An example of a dilution system is one which utilizes a permeable membrane. The dilution ratio acquired from such a system would depend on the volume flow of the carrier gas stream, the surface area and temperature of the membrane, and the permeability of the membrane to the component of interest.

5.11.3.3.7 Procurement guidelines. Upon purchase of the analyzer and associated support equipment, certain procedures should be followed which permit the operator to determine the adequacy of the equipment. The analyzer system must ultimately meet the specifications outlined in section 5.11.1.4. To determine the acceptability of the analyzer, the operator must do one of two things upon purchase of the instrument: 1. Acquire and review the manufacturer's bench test data. Even more preferable is the viewing of the actual bench testing at the factory by the operator prior to shipment of the equipment; or 2. Design and perform a bench test which simulates actual operating conditions, generate, and review output data. The latter suggestion requires immense experience on the part of the operator with the specific equipment. It is beyond the scope of this document to define a specific bench testing process, the extent of which is dependent on the time and economic factors specific to the system at hand, e.g. the necessity for the system to successfully meet the performance testing requirements within a given time schedule would alter bench testing requirements.

Prior to installation of the sampling interface and recording equipment, the operator should simulate a typical operating sampling condition, make several measurements, and study the validity of the output data. Whenever quantitative measurements are not practical, the operator should make a visual inspection of each component to locate obvious defects and/or malfunctions.

The calibration gas mixtures must be checked upon receipt using Method 6 measurements. Nominal concentrations of 0 percent of span, 50 percent of span, and 90 percent of span must be acquired. The average concentration value for each mixture, based on at least three measurements taken at least 24 hours apart, should not differ from the stated concentration value by more than 5 percent.

Any of the components of the system which do not meet acceptable quantitative or qualitative limits should be rejected **prior** to installation. Report and correct any malfunctions, making this information available to all operating personnel.

5.11.3.4 Installation and Instrument Check Guidelines--Because each system is usually specifically designed to meet the requirements at the stack in question, it is recommended that the system design engineer or manufacturing representative take the responsibilities of installation and initial system checkout at the site. Also due to the uniqueness of each system, it is advisable for the operator(s) of the system to be present at the installation and to actively participate in the system testing. With this experience and a detailed operations and maintenance manual, the operator should be able to trouble shoot, define, and resolve most of the problems he may encounter during continuous operation. If the operator is not skilled in the areas of electronics or chemistry, skilled personnel should be available at all times to aid in resolving problems with the minimum of downtime.

Of utmost importance during the installation and initial system testing is that each step and the results be well documented at the front of the Operation and Maintenance Logbook which should be updated daily by the operator. Installation specifications as stated in Performance Specification 2 are reprinted in section 5.11.1.4.

For sampling of sources where the effluent gases cannot be assumed to be nonstratified, Performance Specification 2 (section 5.11.1.4) requires that one of the following measures be taken:

1. The procurement and installation of either a continuous oxygen or a continuous carbon dioxide monitoring system which meets the requirements of Performance Specification 3 (reproduced in appendix A of this document).
2. The procurement and installation of extractive SO_2 monitoring systems using multipoint sampling probes or in-situ pollutant monitoring systems that sample or view emissions which are consistently representative of the total emissions for the entire cross section.

The continuous measurement of oxygen can be accomplished with analyzers utilizing either the paramagnetic technique or a zirconium element. Both of these systems require a clean, dry sample which indicates the need for a sample interface system such as described below in section 5.11.3.3.4. There are no major interferences when using either of these methods. However, problems do exist if particulate matter is allowed to build up in the lines or if there are leaks into the system.

The continuous measurement of carbon dioxide is most commonly achieved with a nondispersive infrared analyzer. The problems and error sources associated with this technique are discussed below in section 5.11.3.3.4.

Research and development of multipoint probes has not yet reached a point where they are readily available to the user. Reference 4 provides a detailed description of errors due to non-stratification and the ways in which the use of multipoint probes will alleviate many of the inaccuracies caused by point source continuous monitoring.

Some general statements which apply to most in-situ and extractive systems unless specified otherwise are listed below. In some cases the manufacturer will make recommendations as to the correct procedures. If not, the experience of the operator and/or installation personnel will play an important role in the success of the system.

The statements are as follows:

1. Temperatures outside the ambient temperature limits of the analyzer may necessitate the use of special environmental control equipment. This equipment should be set up and tested for an undisturbed operating period of at least 1 month before installation as support equipment in the system. The environment during the testing period should be similar to the extreme environmental conditions to be experienced at the analyzer location. During this test period, the temperature at the analyzer location should be measured and recorded continuously or at intervals which suffice in determining that the temperature requirements of the analyzer will be maintained.
2. Mount the analyzer horizontally or vertically as recommended by the manufacturer.
3. Depending on the specific location of the analyzer and the analyzer's sensitivity to vibration, precautions may or may not need to be taken to dampen vibrations to which the analyzer may be subjected. One suggestion is to use foam rubber or the equivalent to isolate the instrument from the mounting platform.
4. Typically, sample handling systems for extractive monitors will incorporate the following:

a. Valves to permit selection of gas sample, zero calibration gas or upscale calibration gas.
b. needle valve inlet in sample line for flow adjustment,
c. flow meter for flow measurement and/or indication of flow stoppage,
d. filters and filter holders.

Each of the above should be checked for cleanliness, proper operation, and no undue disruption of air flow.

5. The layout of the equipment can be very important to the operator's efficiency. A suggestion in this area is that the recorder be near enough to the amplifier/control section so that the operator can easily observe the response to adjustments of the controls. In the majority of systems the recorder response should be observed rather than the meter response on the control panel.
6. The type of pump chosen for the gas sampling in an extractive system will dictate the location of the pump. A simple water or air aspirator can be placed downstream of the analyzer and will exhibit distinct advantages over diaphragm and bellows pumps since aspirators have no internal working parts and are less prone to failure (ref. 12).

5.11.3.5 Performance Testing--The performance specification test procedures presented in section 5.11.1.5 are reproduced from Appendix B as published in the Federal Register, October 6, 1975. The testing procedures include the following independent tests:

- Calibration test
- Field test for accuracy (relative), zero drift, and calibration drift
- Field test for response time

5.11.3.5.1 Calibration test. This test consists of an analysis of the calibration gas mixtures (if used in the system in question) and a calibration of the complete measurement system either in the laboratory or in the field. The latter is preferred. Nominal concentrations of 50 percent and 90 percent of span are recommended. The method of analysis is as directed by Method 6. The analysis must be accomplished within 2 weeks prior to start-up of the system with the objective being to "demonstrate (the calibration gases) to be accurate and stable," (section 5.11.1.2). Alternate methods may be acceptable if approved by the enforcement agency. Record all results on a form as shown in figure 5.11.4.

The entire system is calibrated with a series of five non-consecutive readings for each concentration of span gas, e.g., 50 percent, 90 percent, 50 percent, 90 percent, etc. This method is subject to the particular operation of the system in question. Alternative procedures may be acceptable as recommended by the manufacturer and approved by the enforcement agency. Record all data on a form such as shown in figure 5.11.5.

5.11.3.5.2 Field test for accuracy (relative), zero drift and calibration drift. This test extends over a 2-week period after the measurement system has been installed and started up per the manufacturer's directions. First the operator must offset the zero setting by at least 10 percent so that the negative zero drift characteristic, if any, of the analyzer in question can be quantified. The system should be operated for one week (168 hours) in a normal operational manner. This is called the conditioning period.

The conditioning period is immediately followed by a 168-hour operational test period when the system is on line at all times except during calibration or backflushing of the

ANALYSIS OF CALIBRATION GAS MIXTURES

DATE ______________________________

REFERENCE METHOD USED __________

INITIALS ____________

Calibration Gas Mixture "A":

Cylinder or cell designation________________

Test No. 1 _____________ ppm
Test No. 2 _____________ ppm
Test No. 3 _____________ ppm

Total _____________ ppm

Average = $\frac{\text{Total}}{3}$ = __________ ppm

Calibration Gas Mixture "B":

Cylinder or cell designation________________

Test No. 1 _____________ ppm
Test No. 2 _____________ ppm
Test No. 3 _____________ ppm

Total _____________ ppm

Average = $\frac{\text{Total}}{3}$ = __________ ppm

Figure 5.11.4 Sample data form for the analysis of the calibration gas mixture.

CALIBRATION ERROR TEST DATA

DATE ____________________

OPERATOR ____________________

CALIBRATION GAS MIXTURE "A": (_______ ppm)*

Reading	Time	Measurement Sys. Reading		d_A**	d_A^2
		Volts	ppm		
1					
2					
3					
4					
5					
SUM 1	▨	▨	▨		▨
SUM 2	▨	▨	▨	▨	

CALIBRATION GAS MIXTURE "B": (_______ ppm)*

Reading	Time	Measurement Sys. Reading		d_B**	d_B^2
		Volts	ppm		
1					
2					
3					
4					
5					
SUM 3	▨	▨	▨		▨
SUM 4	▨	▨	▨	▨	

---

*Average value determined in analysis of calibration gas mixtures.

**d = Difference = Average Value (ppm) - Measurement Syst. Reading (ppm)

Figure 5.11.5 Sample log sheet for calibration error test data.

sample lines and other support equipment. If, at any time during this second period, monitoring is interrupted for maintenance procedures, the operational testing time up to the interruption must be noted in the records and repeated (section 5.11.1.6).

The field test for accuracy requires that a minimum of nine SO_2 concentration measurements be taken in accordance with the procedures stated in either Method 6 or 8 depending upon the regulations for the particular source in question. The sampling period should be 1 hour. In all sampling cases the Reference Method sampling probe should be placed as near as possible to the sampling point of the system in question. Record this test data on a form such as demonstrated in figure 5.11.6.

Note: It is recommended that a chemist be available on site to analyze the sample immediately following the sample recovery. This will greatly enhance the efficiency of the testing procedures.

If the basis (wet or dry) for the continuous measurement system is inconsistent with the Reference Method measurements, simultaneous moisture tests should be performed and a correction factor determined. Report the moisture test procedures and data along with the correction factor calculations in the performance test logbook. The column labeled "Reference Method ppm" in figure 5.11.6 is designed for recording the reference method data after the correction factor has been applied.

The field test for the 2-hour zero drift and 2-hour span drift consists of an accumulation of 15 sets of data at 2-hour intervals each. The zero and span values can be produced by pre-tested calibration gases, simulated using equivalent gas cells, or simulated electrically or mechanically within the analyzer if approved by the enforcement agency. The 2-hour intervals must not overlap and do not have to be consecutive.

OPERATIONAL TEST DATA

START:
DATE________________
TIME________________

END:
DATE________________
TIME________________

OPERATOR(S):
____
____

ACCURACY DETERMINATION:

Test No.	Oper. Init.	Date	Time	Ref. Method (ppm)	Analyzer Average			d_i *	d_i^2
					Interval	Volts	ppm		
1									
2									
3									
4									
5									
6									
7									
8									
9									
SUM 5	▨	▨	▨	▨	▨	▨	▨		▨
SUM 6	▨	▨	▨	▨	▨	▨	▨	▨	
SUM 7	▨	▨	▨		▨	▨	▨	▨	▨

[*] d = Difference = Analyzer Average Value (ppm) - Reference Method Value (ppm)

Figure 5.11.6 Sample data form for operational test.

OPERATIONAL TEST DATA

2-HOUR ZERO AND CALIBRATION DRIFT DATA:

Test No.	Oper. Init.	Date	Time		Zero Reading	ΔZ	ΔZ^2	Span Reading	Span Drift	C	C^2
			Begin	End							
1											
2											
3											
4											
5											
6											
7											
8											
9											
10											
11											
12											
13											
14											
15											
SUM 8	▨	▨	▨	▨	▨		▨	▨	▨	▨	▨
SUM 9	▨	▨	▨	▨	▨	▨		▨	▨	▨	▨
SUM 10	▨	▨	▨	▨	▨	▨	▨	▨	▨		▨
SUM 11	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	

Figure 5.11.6 (Cont.) Sample data form for operational test.

OPERATIONAL TEST DATA

24-HOUR ZERO AND CALIBRATION DRIFT DATA:

Test No.	Oper. Init.	Adjustment		Zero Conc.	Zero Reading		ΔZ_{24}	ΔZ_{24}^2	Span Reading		C_{24}	C_{24}^2
		Date	Time		After Adj.	24 hours			After Adj.	24 hours		
1												
2												
3												
4												
5												
6												
7												
SUM 12	▨	▨	▨	▨	▨	▨		▨	▨	▨	▨	▨
SUM 13	▨	▨	▨	▨	▨	▨	▨		▨	▨	▨	▨
SUM 14	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		▨
SUM 15	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	

Figure 5.11.6 (Cont.) Sample data form for operational test.

Record the readings (fig. 5.11.6). Definitions of symbols is found in Appendix B of this document.

During the field testing, zero and span calibration corrections and adjustments are permitted only once every 24 hours. Intervals shorter than 24 hours may be approved if recommended by the manufacturer. The values given by zero and span before and after the 24-hour interval adjustments are made should be measured and recorded as shown in figure 5.11.6 Automatic calibration systems may be used and their corrections can be made at any time.

5.11.3.5.3 Field test for response time. This test should be accomplished with the entire system in normal operation as specified by the manufacturer's instructions. Zero gas is introduced at the probe or as close to the probe as possible. When the output reading has stabilized, a span gas mixture of known concentration is injected at the same point that the zero gas had been injected. The recorded response time is the time between the switching to a span gas and a stable output at the span gas value. The span gas used for this test should be 70 to 90 percent of span. This sequence of operation should be repeated three times and the results recorded on a log sheet as shown in figure 5.11.7.

5.11.3.6 Data Reduction, Validation, and Reporting--Of utmost importance during the performance testing is that all test data are logged correctly and directly upon acquisition of the data. The figures referred to in the previous sections should all be included in a single performance testing logbook in chronological order. Having the data contained in a single notebook will expedite the next steps which are data reduction, validation, and reporting. Figure 5.11.8 shows a simple layout for a form on which the necessary calculations can be made for reporting the test data. Section 5.11.1.6 should be referred to in making those calculations.

RESPONSE TIME TEST DATA

DATE ____________________________

OPERATOR ___________________________

Test No.	Concentration (ppm)	Upscale Response Time (seconds)
1		
2		
3		
SUM 16	▨	
AVERAGE	▨	

Test No.	Concentration (ppm)	Downscale Response Time (seconds)
1		
2		
3		
SUM 17	▨	
AVERAGE	▨	

Figure 5.11.7 Sample data form for response time test.

DATA ANALYSIS REPORT CALCULATIONS

DATE________________________

OPERATOR______________________

CALIBRATION ERROR DETERMINATION "A"

Mean difference $= \frac{\text{Sum 1}}{5} =$ __________ ppm

95% Confidence interval $= \text{C.I.}_{95} = .2776 \sqrt{5(\text{Sum 2})-(\text{Sum 1})^2}$

$=$ __________

Calibration error for "A" $= \frac{|\text{Mean difference}| + \text{C.I.}_{95}}{\text{Avg. calib. gas conc.}} \times 100$

$=$ _____________ percent

CALIBRATION ERROR DETERMINATION "B"

Mean difference $= \frac{\text{Sum 3}}{5} =$ __________ ppm

95% Confidence interval $= \text{C.I.}_{95} = .2776 \sqrt{5(\text{Sum 4})-(\text{Sum 3})^2}$

$=$ ______________ percent

Calibration error for "B" $= \frac{|\text{Mean difference}| + \text{C.I.}_{95}}{\text{Avg. calib. gas conc.}} \times 100$

$=$ ____________ percent

Figure 5.11.8 Sample form for data analysis report calculations.

DATA ANALYSIS REPORT CALCULATIONS

ACCURACY DETERMINATION

Mean difference $= \frac{\text{Sum } 5}{9} =$ __________ ppm

95% Confidence interval $= \text{C.I.}_{95} = .0906\sqrt{9(\text{Sum } 6)-(\text{Sum } 5)^2}$

$=$ __________

Mean reference method value $= \frac{\text{Sum } 7}{9} =$ __________

$$\text{Accuracy} = \frac{|\text{Mean difference}| + \text{C.I.}_{95}}{\text{Mean ref. method value}} \times 100$$

$=$ ______________ percent

ZERO DRIFT (2-hour)

Mean zero drift $= \frac{\text{Sum } 8}{15} =$ __________ ppm

$\text{C.I.(zero)}_{95} = .0382\sqrt{15(\text{Sum } 9)-(\text{Sum } 8)^2} =$ __________

Emission standard = __________ ppm

$$\text{Zero Drift} = \frac{|\text{Mean zero drift}| + \text{C.I.(zero)}_{95}}{\text{Emission Standard}} \times 100$$

$=$ __________ percent

Figure 5.11.8 (Cont.) Sample form for data analysis report calculations.

DATA ANALYSIS REPORT CALCULATIONS

CALIBRATION DRIFT (2-hour)

Mean calibration drift = $\frac{\text{Sum }10}{15}$ = __________ ppm

C.I.(span)$_{95}$ = $.0382\sqrt{15(\text{Sum }11)-(\text{Sum }10)^2}$ = __________

Emission standard = __________ ppm

$$\text{Calibration drift} = \frac{\left|\text{Mean span drift}\right| + \text{C.I.(span)}_{95}}{\text{Emission standard}} \times 100$$

= ______________ percent

ZERO DRIFT (24-hour)

Mean zero drift = $\frac{\text{Sum }12}{7}$ = __________ ppm

C.I.(zero)$_{95}$ = $.1427\sqrt{7(\text{Sum }13)-(\text{Sum }12)^2}$ = __________

Emission standard = __________ ppm

$$\text{Zero drift} = \frac{\left|\text{Mean zero drift}\right| + \text{C.I.}_{\text{(zero)}_{95}}}{\text{Emission standard}} \times 100$$

= __________ percent

Figure 5.11.8 (Cont.) Sample form for data analysis report calculations.

DATA ANALYSIS REPORT CALCULATIONS

CALIBRATION DRIFT (24-hour)

Mean calibration drift = $\frac{\text{Sum 14}}{7}$ = __________ ppm

C.I. $(\text{span})_{95} = .1427 \sqrt{7(\text{Sum 15})-(\text{Sum 14})^2}$

Emission standard = __________ ppm

$$\text{Calibration drift} = \frac{|\text{Mean span drift}| + \text{C.I.}(\text{span})_{95}}{\text{Emission standard}} \times 100$$

= ____________ percent

RESPONSE TIME

System reponse time = slower response time = __________.

Percent deviation from slower time

$$= \frac{\text{avg. upscale - avg. downscale}}{\text{slowest time}} \times 100$$

= __________ percent

Figure 5.11.8 (Cont.) Sample form for data analysis report caculations.

The personnel responsible for doing the data analysis for the performance test should date the data analysis form and initial it. Preferably this personnel will have participated in the field testing, hence will be familiar with the data and its origin.

The first determination which must be made is that of the calibration error which applies to the calibration gas mixtures. In figure 5.11.8 the terms "A" and "B" refer to the mid-range gas mixture and the span range gas mixtures, respectively. For each error determination the mean difference between the actual value of the gas mixture (as resulted from a Method 6 test on the mixture within at least one week prior to the calibration test) and the value of the gas mixture measured by the continuous analyzer system. These are calculated using the following equation:

$$\bar{X} = \frac{1}{n} \sum_{i=1}^{n} X_i \qquad (1)$$

where X_i = individual difference values

$\sum$ = sum of the individual values

$\bar{X}$ = mean difference value

and n = number of data points.

More specifically, the mean difference for each calibration value is calculated in this way (i.e., $\bar{d} \equiv \bar{X}$)

$$\bar{d}_A = \frac{\sum_{i=1}^{5} (\text{Measurement system reading}_i - \text{actual value of "A"})}{5} \qquad (2)$$

and

$$\bar{d}_B = \frac{\sum_{i=1}^{5} (\text{Measurement system reading}_i - \text{actual value of "B"})}{5} \quad .(3)$$

The 95 percent confidence interval, as defined in section 5.11.1.6,* is calculated using the following equation:

$$C.I._{95} = \frac{t_{.975}}{n\sqrt{n-1}} \sqrt{n\left(\Sigma X_i^2\right) - \left(\Sigma X_i\right)^2} \qquad (4)$$

where ΣX_i = sum of all data points,

$t_{.975} = t_{1-\alpha/2}$

and $C.I._{95}$ = 95 percent confidence interval estimate of the mean value of the differences.

The value for $t_{.975}$ is dependent on the number of data points which, in the case of the calibration test, is five (n=5) for each mixture. A table from which $t_{.975}$ can be drawn for values of n up to 16 is given below (table 5.11.2).

The calibration error for each gas mixture is determined in the following manner:

$$\text{Calibration error} = \frac{|\text{Mean difference}| + C.I._{.95}}{\text{Avg. calib. gas concentration}} \times 100. \qquad (5)$$

---

[*] The value CI_{95} defined in section 5.11.1.6 is actually the value which, when added to the mean, defines the upper limit of the 95 percent confidence interval.

Table 5.11.2 Values for $t_{.975}$

n	$t_{.975}$	n	$t_{.975}$
2	12.706	10	2.262
3	4.303	11	2.228
4	3.182	12	2.201
5	2.776	13	2.179
6	2.571	14	2.160
7	2.447	15	2.145
8	2.365	16	2.131
9	2.306		

This error is reported in percent and is not to exceed 5 percent of each calibration gas mixture value (sec. 5.11.1.4).

The accuracy determination, reported in percent, is based on the values recorded on the Operational Test Data Form (fig. 5.11.6) as a result of the Method 8 sampling and analysis. The equation used for the determination is:

$$\text{Accuracy} = \frac{|\text{Mean difference}| + \text{C.I.}_{.95}}{\text{Mean reference method value}} \times 100 \qquad (6)$$

where Mean difference = the average difference between the Reference Method measurement values and the corresponding interval averaged data from the continuous measurement system,

and Mean reference method value = the value calculated using equation (1).

The accuracy should not exceed 20 percent as specified in section 5.11.1.4.

The 2-hour zero drift, 2-hour calibration drift, 24-hour zero drift, and 24-hour calibration drift values are each calculated using the same equation:

$$\text{Drift} = \frac{\left|\text{Mean drift}\right| + \text{C.I.}_{.95}}{\text{Emission standard}} \times 100 \qquad (7)$$

where Drift is reported in percent of emission standard,

$\text{C.I.}_{.95}$ is calculated as shown in equation (4),

and Emission standard is that which applies to the source in question.

The limits of the drifts, as set forth under Performance Specification 2 in section 5.11.1.5, are as follows:

Zero drift (2 hour) . . . . $\leq$ 2 percent of span

Zero drift (24 hour) . . . . $\leq$ 2 percent of span

Calibration drift (2 hour). . . $\leq$ 2 percent of span

Calibration drift (24 hour) . . . $\leq$ 2.5 percent of span

The response time calculation is based on data documented on the form such as shown in figure 5.11.7. The system response time is determined by the slower average response time (either the measured upscale response time or the downscale response time) and should not exceed 15 minutes. The specifications (section 5.11.1.4) require that the response time be reported as the percent deviation from the slower time which is calculated in this way:

$$\text{Percent deviation from slower time} = \frac{\text{Avg. upscale - avg. downscale}}{\text{slower time}} \times 100. \quad (8)$$

5.11.3.7 General Operation and Maintenance Procedures for Non-Compliance Monitoring--The performance test as described above serves three purposes. They are:

1. Determines the adequacy of the installed system in meeting the performance specifications detailed in section 5.11.1.4.
2. Provides a 2-week period of uninterrupted data collection which, if the system meets the performance specifications, can be used to determine the compliance of the stack being monitored to existing regulations.
3. Provides a basis for determining the operation and maintenance procedures which will be required by the continuous system as it is installed at the location in question.

This section of the quality assurance document will expound on various aspects of purpose number 3. Because Performance Specification 2 is applicable to such a wide variety of sulfur dioxide monitoring systems, only general guidelines on operation and maintenance can be provided here for the monitoring system when it is not being subjected to the performance test and is not being used for compliance monitoring.

Unless otherwise specified, the data from the continuous monitoring system should be reduced, validated and reported on a regular basis. Generally one hour average computations are required. These computations should be made using four equally spaced points over a 60 minute period commencing on the hour.

The system must be automatically checked for zero and span drift and adjusted accordingly at least every 24 hours. When the system is not equipped with automatic calibration at zero and span, then a manual check should be made at least twice weekly or as recommended by the manufacturer. A dynamic calibration, the input of at least two non-zero calibration gases and appropriate adjustments made, and a response time check should be performed routinely once every two weeks. Depending upon the drift characteristics of the particular system in question, each of these statements may or may not have to be altered as the operator gains experience with the analyzer, interface system, and source effluent.

In all cases, calibration gases should be inputted as close to the sampling probe as possible so that the calibration will include the interface system. For those systems where this is not possible, the use of Method 6 or 8 measurements at least once per month is recommended. Calculations and comparisons of the Reference Method data with the corresponding continuous system data would follow the procedures discussed above in sections 5.11.3.5 and 5.11.3.6.

When a dynamic calibration is performed at least twice a month, the use of Method 6 or 8 (refs. 1 and 2) measurements once per quarter is suggested. This would involve taking at least four samples, analyzing them, and comparing the data with the continuous measurement data for the corresponding time period. The comparison calculations would again follow the procedures set forth above.

Manufacturer's recommendations should be followed in performing preventive maintenance on the system in the first weeks of operation. If the system exhibits excessive drifts or if accuracy tests prove the system to be malfunctioning, preventive maintenance procedures should be reevaluated and rewritten in view of the operating experience as discussed below.

5.11.3.7.1 Use of control charts. The use of control charts is highly recommended for three reasons:

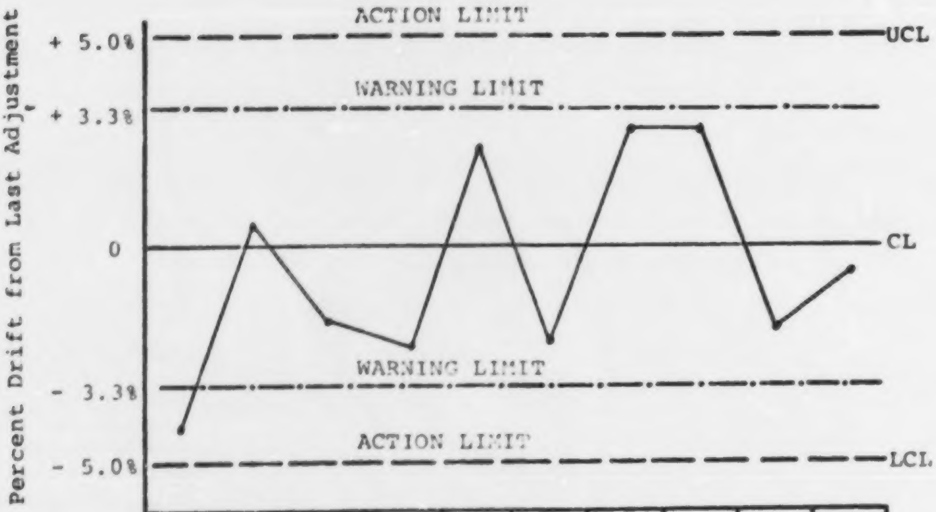
1. They provide an "at-a-glance" description of the operation of the system.
2. They are a visual aid in maintaining consistency in the operation and maintenance procedures.
3. Trends in the monitoring data are obvious with the continued use of control charts and oncoming problems can often be foreseen and avoided.

One example of a possible use of control charts is in determining zero drift trends with a chart as shown in figure 5.11.9. In this example, the UCL (upper control limit) and LCL (lower control limit) used are +5.0 percent and -5.0 percent, respectively. Recommended operating policies could inlcude the following:

1. No single 24-hour zero drift value from the last adjustment should exceed 5 percent without the immediate performance of troubleshooting and correction procedures; and
2. Trouble shooting and correction procedures should be performed if four consecutive checks result in drifts of the same sign.

In addition to determining zero drift trends, other possible applications of control charts include the visual depiction of the mean, the range, or the standard deviation of the following measurement values over several sets of tests:

- accuracy checks
- calibration gas checks



CHECK NO. j	1	2	3	4	5	6	7	8	9	10
DATE/TIME										
OPERATOR										
PROBLEM AND CORRECTIVE ACTION										

Figure 5.11.9 Sample control chart for use in determining trends in zero drift.

- zero/calibration drift (2-hour)
- zero/calibration drift (24-hour)

5.11.3.7.2 Use of operation and maintenance tables. The use of operation and maintenance tables is recommended to increase the operator's efficiency, to provide a visual display of the requirements of the system, and to provide a simplistic means of updating and adding to the routine procedures as the operator gains experience with the system in question. Figure 5.11.10 gives an example of such a table.

The operation and maintenance table should be formulated by the operator who will have the major responsibility for the system. The basis for the table should be: the maintenance manuals supplied by the various component manufacturers, interaction with the factory representatives at the installation of the system and, most important, personal experience gained during the performance testing and any time thereafter. If possible, the operator should visit the manufacturing facility prior to the shipment of the system and witness the bench testing. Valuable information can be acquiesced at this time which may otherwise be acquired only after several weeks of operation and hours of troubleshooting.

After the original operation and maintenance table is formulated, its usefulness can be extended by a continuous update of the information contained in the table. For instance, upon survey of a month's data, the operator may determine that either more or less frequent calibration is eminent for greater data validity. Or, another case might be extreme drift in the calibration values which would indicate that restandardization of the calibration gas is necessary.

OPERATION AND MAINTENANCE TIMETABLE

PROCEDURE	Interval Between Performance								
	8 hours	24 hours	72 hours	1 week	2 weeks	1 month	3 months	6 months	1 year
Zero calibration	✓								
Span calibration	✓								
Dynamic calibration			✓						
Change desiccant in reference cell								✓	
Inspect filter holder						✓			
Change filter							✓		
Clean sample cell							✓		
Check gaskets for deterioration							✓		
Check optics for cleanliness						✓			
Check refrigeration system						✓			
Check needle valves						✓			
Check probe heating system						✓			
Analyze calibration gas							✓		

Figure 5.11.10 Sample operation and maintenance table.

5.11.4 Auditing Procedures

The proper planning and implementation of an auditing program allows the enforcement agency to estimate data quality in terms of precision and accuracy at a given level of confidence. To realize maximum benefits from an auditing program, the auditing procedures should be conducted independently of the routine operation of the sampling network. That is, the audit checks should be made by individuals other than the regular operator and using calibration standards supplied and tested by the auditing agency. Furthermore, the audit checks should be performed without any special preparation or adjustment of the system.

In conjunction with the special checks required during performance testing and assuming that all routine calibration and maintenance checks are performed judiciously, three auditing checks will be sufficient to properly assess data quality.

1. A visual check of the sampling interface, analyzer, and data recording system.
2. The extraction and analysis of at least four samples using the procedures outlined in Method 6 or 8 (refs. 1 and 2) and a comparison of this data with the corresponding data for the same sampling period as recorded by the continuous analyzer system.
3. A data processing check to evaluate data reduction and computation errors.

An auditing level of three checks (n=3) per performance test period and one check (n=1) every 6 months during noncompliance monitoring is used here for illustration purposes. This assumes that sampling is carried out continuously for non-conformance monitoring purposes and that the 2-week performance test period and compliance monitoring are synonymous. This would result in a minimum auditing level of three checks (n=3) for a lot size of 12 (N=12) for data reported quarterly. The enforcement agency will specify the actual auditing level required to meet specific monitoring needs.

Direction for performing each of the checks are given here.

5.11.4.1 Visual Checks--The auditor should prepare a standard check sheet for each individual system which lists all of the major components of the system and the parameters which can and should be visually assessed. Such parameters would include:

- Proper operation of the data recording system.
- Proper location and position of the sampling probe.
- Any major changes in the sample interface system.
- Cleanliness of system components.
- Undue deterioration of system components.

The list would, of course, be more specific in the items listed but these are general guidelines for what should be included. Any changes made in the system or information resulting from an increased familiarity with the system should be reflected in revisions of the list.

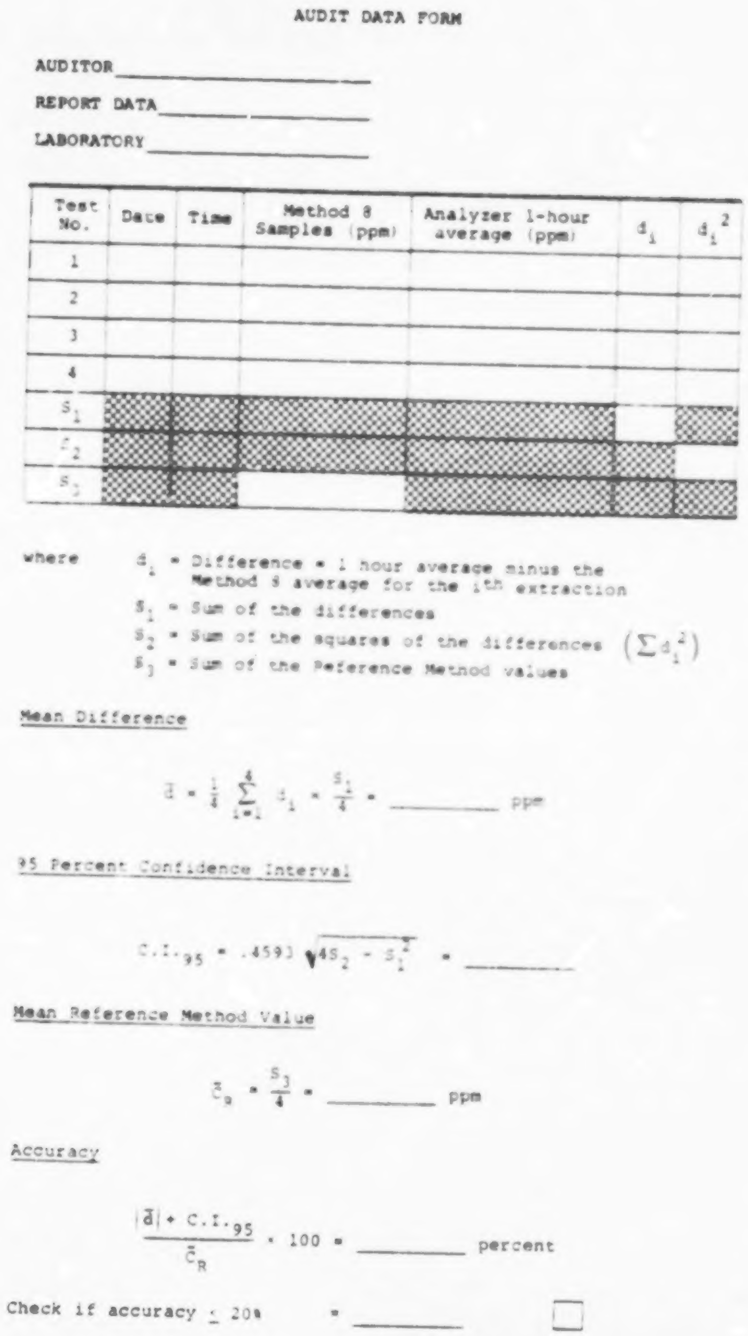
5.11.4.2 Redundant Monitoring Using Appropriate Reference Method--The auditor or auditing crew, other than the regular operator(s) of the system, must extract at least four samples using the sampling techniques discussed in reference 1 for sampling periods of 1 hour each. The manual method probe tip must be placed adjacent to the continuous system probe tip. The samples should be analyzed by the auditor or an independent laboratory. The data are documented and submitted for assessment. Data from the continuous system which was recorded simultaneously with the manual sampling should be reduced from the stripchart or magnetic tape recording system.

Results from both the Method 8 sampling and the continuous system measurements should then be logged on an Audit Data Form, an example of which is shown in figure 5.11.11. The calculations given on the Audit Data Form correspond to those specified in section 5.11.1.6. If the accuracy calculated on the audit data form exceeds 20 percent, corrective action should be taken by the regular operator(s) to determine the cause of the extreme inaccuracies and the auditing schedule should be changed to allow for more frequent audits.

An alternate to the manual extraction and analysis of samples is the measurement of calibration standards. These calibration standards used in implementing an audit check should be prepared independently of the normal operations and analyzed by Method 6 within 2 weeks prior to use or demonstrated to be accurate and stable in some equivalent manner. The results of the analysis should be well documented and available for use in the assessment of the data from the continuous monitoring system.

The calibration standards should be inputted at the sampling probe or as close to the sample probe as possible. In the case of in-situ optical sensors, special calibration cells can be tested prior to the audit and inserted in the optical pathlength of the sensor as specified by the manufacturer. Allow the system to stabilize and record the measurement.

The use of three different upscale values of calibration standards is recommended for audit purposes. The following



AUDIT DATA FORM

AUDITOR______________________

REPORT DATA____________________

LABORATORY____________________

Test No.	Date	Time	Method 8 Samples (ppm)	Analyzer 1-hour average (ppm)	d_i	d_i^2
1						
2						
3						
4						
S_1	▨	▨	▨	▨		▨
S_2	▨	▨	▨	▨	▨	
S_3	▨	▨		▨	▨	▨

where d_i = Difference = 1 hour average minus the Method 8 average for the ith extraction

S_1 = Sum of the differences

S_2 = Sum of the squares of the differences $\left(\sum d_i^2\right)$

S_3 = Sum of the Reference Method values

Mean Difference

$$\bar{d} = \frac{1}{4}\sum_{i=1}^{4} d_i = \frac{S_1}{4} = \_\_\_\_\_\_\_\_ \text{ ppm}$$

95 Percent Confidence Interval

$$C.I._{95} = .4593\sqrt{4S_2 - S_1^2} = \_\_\_\_\_\_\_\_$$

Mean Reference Method Value

$$\bar{C}_R = \frac{S_3}{4} = \_\_\_\_\_\_\_\_ \text{ ppm}$$

Accuracy

$$\frac{|\bar{d}| + C.I._{95}}{\bar{C}_R} \times 100 = \_\_\_\_\_\_\_\_ \text{ percent}$$

Check if accuracy $\leq$ 20% = ________ ☐

Figure 5.11.11 Sample audit data form.

control limits should be exercised in analyzing the audit data: If the difference between any one continuous measurement system value and the predetermined calibration standard value is greater than 20 percent of the latter value or if the average of the three differences exceed 10 percent, checks should be made to determine the cause of the inaccuracies, corrective action(s) taken, and the audit procedures repeated.

The actions which must be taken might include:

1. Perform a regular zero and span check with the calibration standards used routinely.
2. If, after number 1 has been performed, the audit value still proves inconsistent with the known concentration value, a dynamic calibration should be performed with the calibration standards used routinely.
3. Repair the system or perform maintenance, as required, based on the calibration results.
4. Resume normal operation only after the results of an audit check prove satisfactory.

5.11.4.3 Data Processing Check--Independent checks for data processing errors should be incorporated into every auditing program. The checks should be made by an individual other than the operator responsible for the original data reduction, calculations, and reporting. The procedures for making the data processing checks are highly dependent upon the sophistication of the data acquisition system. In this section, two types of systems will be discussed and general procedural guidelines set forth. They are stripchart recording systems and magnetic tape recording systems.

5.11.4.3.1 Stripchart recording systems. The auditor must check the following items if the continuous analyzer is interfaced with a stripchart recording system:

1. Accuracy with which the operator reads the data from the stripchart and records the data on a logsheet.
2. Equations used to transform the analog voltage data to meaningful parts per million units.
3. Averaging process to obtain the required one-hour averages.
4. Method of data validation using calibration data as recorded on stripcharts and determinations of system malfunctions.

Because most of the transfer equations which would be required for a continuous SO_2 monitoring system are relatively simple, most errors will be the result of carelessness on the part of the person reducing the data from the stripchart. Systematic errors should be eliminated by careful training of the operator as to the treatment of roundoffs and illegible data.

The auditor should reduce data for a randomly chosen 1-week period. The check should be made starting with the raw stripchart data and ending with the recording of the 1-hour average SO_2 measurements in concentration units of parts per million on a form similar to or the same as those forms used routinely by system operator. A comparison of the auditor's measurement values with the originally determined values should show a difference of less than ± 3 percent. If determined necessary by the enforcement agency, all data since the last audit may have to be checked and corrected if the difference exceeds ± 3 percent.

5.11.4.3.2 Magnetic tape recording system. If the data acquisition system consists of a magnetic tape recorder, then the first parameter listed in section 5.11.4.3.1 is not applicable. It can generally be assumed that the error in reducing data from magnetic tape by a computer is minimal. However, the latter two parameters which have to do with transfer questions and data validation are very much applicable. The auditor must determine if the programming handles the raw data such that the final output reflects the measured quantities. Some of the more sophisticated systems will use the calibration data to generate new adjustment equations and will apply these equations directly to the raw data. The auditor must study the raw data (in voltages) and manually apply the appropriate equations to arrive at the average sulfur dioxide concentration over the recording interval in concentration units. The auditor's data should not differ more than 1 percent from the computerized data report. If the difference is greater than 1 percent, the entire system must be analyzed and the discrepancies found and rectified.

3.0 FUNCTIONAL ANALYSIS

3.0 FUNCTIONAL ANALYSIS

Performance Specification 2 defines the performance specifications and specification test procedures for continuous monitors of sulfur dioxide and oxides of nitrogen from stationary sources. As stated before, this quality assurance document is treating only the determination of sulfur dioxide. The performance specification states that SO_2 monitoring systems must meet certain requirements but does not specifically state the components of the system. For this reason, the functional analysis will be general and will exemplify a systems approach which might be taken to formulate a functional analysis of a particular system.

This test method has been subjected to no collaborative tests and relatively few performance tests (refs. 13 through 17), so quantitative components is not available. Engineering judgments, based on considerable experience with both stack or air quality sulfur dioxide analyzers and the associated sampling and interface systems, were used in lieu of collaborative test data in some of these areas of variable evaluation. The subject of error analysis is discussed in references 18 and 19.

Continuous systems for monitoring sulfur dioxide in stack emissions can consist of several different component combinations. Basically though, the systems can be divided into two categories, in situ and extractive. Both types of systems are shown graphically in figures 5.11.12 and 5.11.13, respectively.

3.1 DEFINITION AND DISCUSSION OF ERROR SOURCES

The various phases of the continuous measurement will each contain numerous sources of error. Some errors can be eliminated by a conscientious system operating staff, while others are inherent within the system and can only be controlled. The paragraphs below discuss the components of error for both types of systems. The standard deviation stated in this section are estimates given for illustrative purposes only, and have not been substantiated by sufficient field data to be stated as fact.

3.1.1 In-Situ Monitoring Systems

Based on the fact that in-situ monitoring systems avoid the need for extracting a gas sample from the stream, such systems do not manipulate the sample of gas being measured. This statement can lead to two conclusions: 1. in-situ systems are simpler than extractive systems, and 2. the sources of error will be fewer. Both of these conclusions are valid but must be discussed further for one to fully understand all implications.

First, the in-situ systems are generally simpler in that they contain fewer major components and are usually based on straightforward electro-optical principles. The sophistication of the system comes into play in the engineering, design, and fabrication of a system which can withstand the adverse environment after installation and which will, indeed, provide a measurement which is indicative of the concentration of SO_2 in the total emissions.

Second, the sources of error will be fewer with an in-situ system. However, in defining the error components, the analyst will determine that the error due to each of these

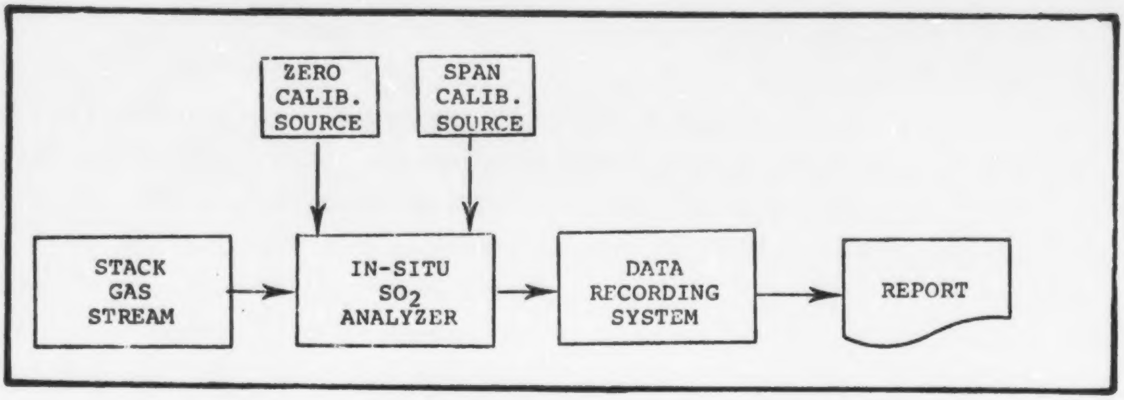

ZERO CALIB. SOURCE
SPAN CALIB. SOURCE
STACK GAS STREAM
IN-SITU SO_2 ANALYZER
DATA RECORDING SYSTEM
REPORT

Figure 5.11.12 Block diagram of a typical in-situ monitoring system.

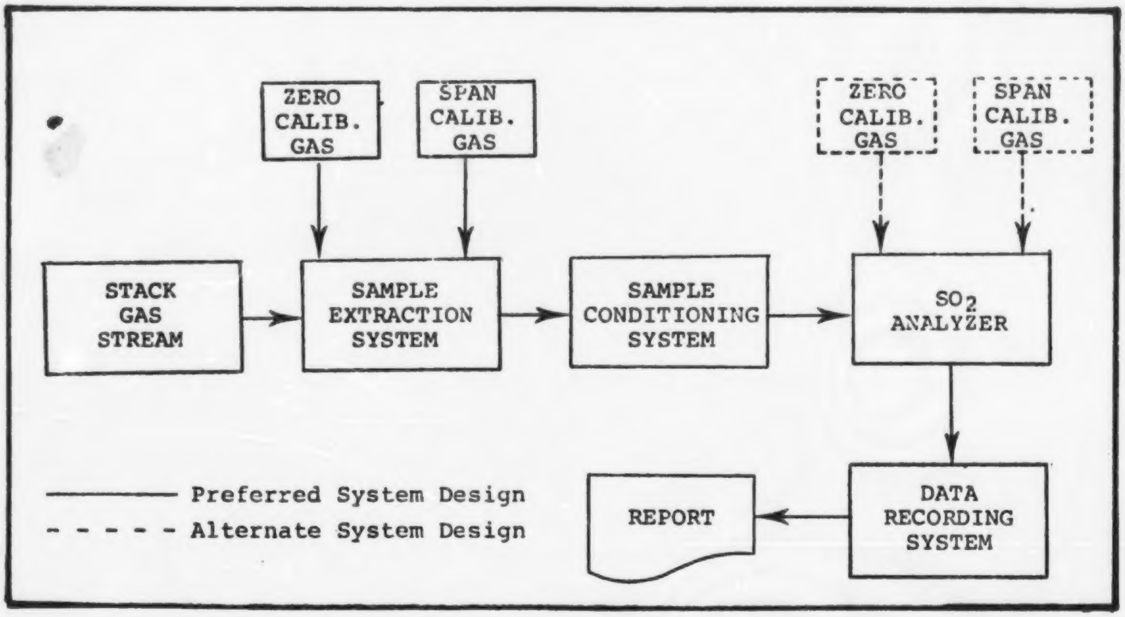

ZERO CALIB. GAS
SPAN CALIB. GAS
ZERO CALIB. GAS
SPAN CALIB. GAS
STACK GAS STREAM
SAMPLE EXTRACTION SYSTEM
SAMPLE CONDITIONING SYSTEM
SO_2 ANALYZER
Preferred System Design
Alternate System Design
REPORT
DATA RECORDING SYSTEM

Figure 5.11.13 Block diagram of a typical extractive monitoring system.

components is greater than with extractive systems, and that the overall system error for both types of systems will usually prove to be comparable.

Error sources for in-situ monitoring systems include:

1. Measurement method errors, σ_m;
2. Calibration inadequacies and the associated drift problems, σ_c;
3. Data recording errors, σ_r, and
4. Data processing errors, σ_p.

These major components of the total system error are illustrated with a block diagram in figure 5.11.14 and are discussed below.

3.1.1.1 Measurement Method Errors, σ_m--Assuming that most in-situ monitors are of the electro-optical variety, the following list of error sources is generally applicable.

1. Accumulation of particulate matter on windows. A primary problem with in-situ monitors is the accumulation of particulate matter on the windows of the analyzer case. The particulate matter will block the transmission of light through the windows resulting in a negatively biased response by the photodetector. Two different methods are now used by commercially avilable instruments in an attempt to overcome the problem. The use of dedicated fans that are directed across the face of the windows to avoid the accumulation of particulates is one method. This method has proven partially inaffective due to the unreliability and inefficiency of the fanning system causing a negative error in the final measurement. The second method is the use of a detection module which separates the beam into two sets of

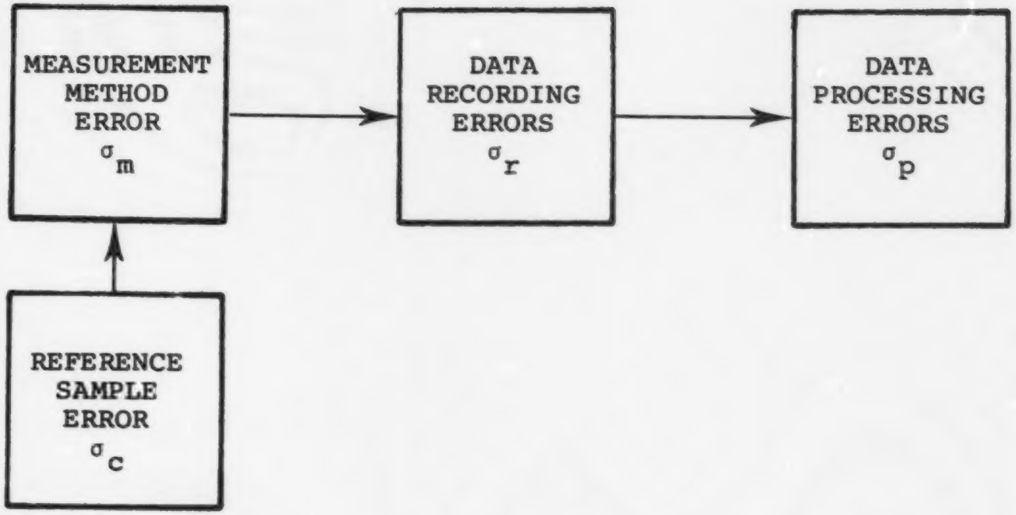

MEASUREMENT
METHOD
ERROR
σ_m
DATA
RECORDING
ERRORS
σ_r
DATA
PROCESSING
ERRORS
σ_p
REFERENCE
SAMPLE
ERROR
σ_c

Figure 5.11.14 Major components of system errors in an in-situ monitoring system.

component wavelengths (ref. 20). One range of wavelengths is absorbed solely by SO_2 and the second range is not absorbed by any of the constituents of the stack gas. The result of this system is to totally discount the effect of the particulate blocking of the transmitted and reflected light. Errors due to this second method would be realized if the chosen wavelengths were indeed absorbed to some degree by a stack gas constituent and would produce a negative bias in the response of the photodetector.

2. Misalignment of the optical components. The misalignment of light sources, mirrors, diffraction gratings, and photodetectors is another major source of error in in-situ systems. Design objectives for any in-situ system must include the fabrication of an instrument with as few moving parts as possible and that is insensitive to the constant vibrations and drastic temperature differences to which the instrument will be subjected when installed on a stack. A misalignment of the optical components will cause a loss of light intensity which will in turn result in a negative bias in the system measurements.
3. Detector insensitivity. The detector must contain filters so as to block detection of wavelengths other than the wavelengths of interest. In the event of faulty filters or a secondary problem, loss of detector sensitivity, the output readings from the system will be biased. Assuming that the

deteriorated filters will allow other wavelengths of light to pass through the analyzer secton and be included with the proper wavelengths in determining an intensity proportional to the concentration of sulfur dioxide, the existence of deteriorated filters will cause a positive bias in the output signal. In the event of a loss of sensitivity of the detector to the intensity of the light passing through the analyzer, the output signal will be negatively biased.

4. Interferences by other constituents of the stack gas. Water vapor and other constituents of the stack gas can cause interference in the electro-optical measurement of SO_2 with an in-situ monitor. Careful selection of the absorption peak chosen for a particular application can minimize interferences.

5. Change in the absorption characteristics of the sulfur dioxide component of the stack gas. According to one study, references 7 and 15, temperature variations of the gas sample in the slot can broaden the spectrum seen by the spectrometer. Reported in the study was that a 6°C change in stack gas temperature alters the output signal by 3 percent. Such a radical temperature effect will most likely occur only at very high stack gas temperatures and, if the stack gas temperature range is known, appropriate correction factors can be applied to the data.

The standard deviation of the measured SO_2 concentration as a result of error due to each of the above-mentioned sources cannot be assigned in this document because of the lack of sufficient field test data to support individual variable analysis. However, a standard deviation of the measured SO_2 concentration resulting from all measurement method errors is estimated to be 10 percent of the true concentration in parts per million. This estimate is given for illustrative purposes only. The standard deviation for a specific system must be determined from performance test data and field operation data for that system.

3.1.1.2 Calibration Inadequacies and the Associated Drift Problems, σ_c--Calibration techniques on an in-situ monitor are generally complicated if performed manually and are less reliable if performed automatically. Supporting this statement are the following problems existing in the calibration of in-situ monitors:

1. The manufacture and testing of calibration cells for use in calibrating in-situ monitors is more complex than the use of cylinder gas in calibrating extractive monitors. The pathlength from the cell to the photodetector and the amount of SO_2 in the cell are both variables in determining the span gas concentration as measured by the analyzer.
2. The pathlength between the photodetector and the light reflected back through the sample stack gas must generally be blocked during calibration. This procedure requires at least one moving part which must be able to function properly regardless of ambient conditions, i.e., vibration, extreme temperatures, etc.
3. If the reference gas cell is calibrated at a given stack gas temperature and is used at another temperature without correction, the data will be erroneous.

4. If the monitor must be calibrated manually, a qualified technician must climb the stack to the location of the monitor to perform the calibration. "Qualified" technician infers that the operator must be trained in the routine calibration and maintenance of the system so that he is aware of any mechanical or electrical problems should they occur (ref. 21).
5. Zero and span drift due to the analyzer's sensitivity to pressure and temperature changes between manual or automatic checks will alter the data accuracy. In most cases the data cannot be accurately adjusted based on subsequent calibration data.

For illustrative purposes only an estimated standard deviation, σ_c, of 8 percent is assumed for the true SO_2 concentration as a result of error due to calibration inefficiencies.

3.1.1.3 Data Recording Errors, σ_r--In continuous monitoring, data recording errors can result from inadequate response of the mechanical stripchart recording to varying sulfur dioxide concentration. If magnetic tape recording systems are used, errors in the recorded signal can result from improper amplification of the analyzer output or malfunctions in the recorder. Because of the advanced state-of-art in data acquisition systems, a standard deviation, σ_r, of 2 percent is estimated (for illustrative purposes only) for the effects of data recording errors on the measurement of sulfur dioxide by an in-situ monitor.

3.1.1.4 Data Processing Errors, σ_p--Data processing errors can be avoided through extreme conscientiousness of the data processing personnel. Errors may occur, though, in making accurate estimates of average values on illegible stripchart recordings. Other error sources are:

1. Misreading of calibration data from stripchart recording or raw magnetic tape recording data. This can take the form of data being read as span data when the system has not actually stabilized at a span reading.
2. Carelessness in reading discrete measurement values with the utmost accuracy.
3. Mistakes such as manually reading the correct data and transposing the numerical figures upon recording the data.
4. Calculation errors in determining average concentrations over an extended sampling period.
5. Time shifting of magnetic tape data resulting from improper input of start-time data into the computer or from loss of data without battery carryover for recorder time synchronization with real time (the latter is also applicable to stripchart records).

An estimate of the standard deviation of the measurement value as a result of data processing errors, σ_P, is 3 percent (for illustrative purposes only).

3.1.1.5 Total Standard Deviation, σ_T--All of the error terms discussed above can be considered independent for analysis purposes, hence the total bias in the continuous measurement of sulfur dioxide by in-situ monitors is the algebraic sum of the biases of the individual terms. The variance of the data, σ_T^2, is the sum of the variances of the individual error terms as follows:

$$\sigma_T^2 = \sigma_m^2 + \sigma_c^2 + \sigma_r^2 + \sigma_p^2$$

Using the estimated example values given in the previous paragraphs, $\sigma_T^2 = .0177$ or $\sigma_T = 13.3$ percent of the true concentration of sulfur dioxide. An exact value of σ_T for a particular system can only be determined after a sufficient quantity of field data has been taken and analyzed.

3.1.2 Extractive Monitoring Systems

The variable analysis of extractive monitoring systems can only be accomplished with accuracy after a comprehensive definition of the system components has been made. As depicted in figure 5.11.15, the major components of system error can be divided into five categories:

1. Sampling interface errors, σ_{f_e};
2. Method measurement errors, σ_{m_e};
3. Reference sample errors, σ_{c_e};
4. Data recording errors, σ_{d_e}; and
5. Data processing errors, σ_{p_e}.

Each of the above categories are discussed separately in the paragraphs below.

3.1.2.1 Sampling Interface Errors, σ_{f_e}--The sampling interface consists of the components of a measurement system which extract and in some way modify the gas sample to be analyzed as a representative sample of the total stack gas. In accomplishing the objective of the interface system, which is to supply a sample with characteristics compatible with the analyzer in use, the interface system may perform any of the following operations in addition to the extraction: transportation, filtration, or conditioning of the sample in terms of temperature or water content reduction.

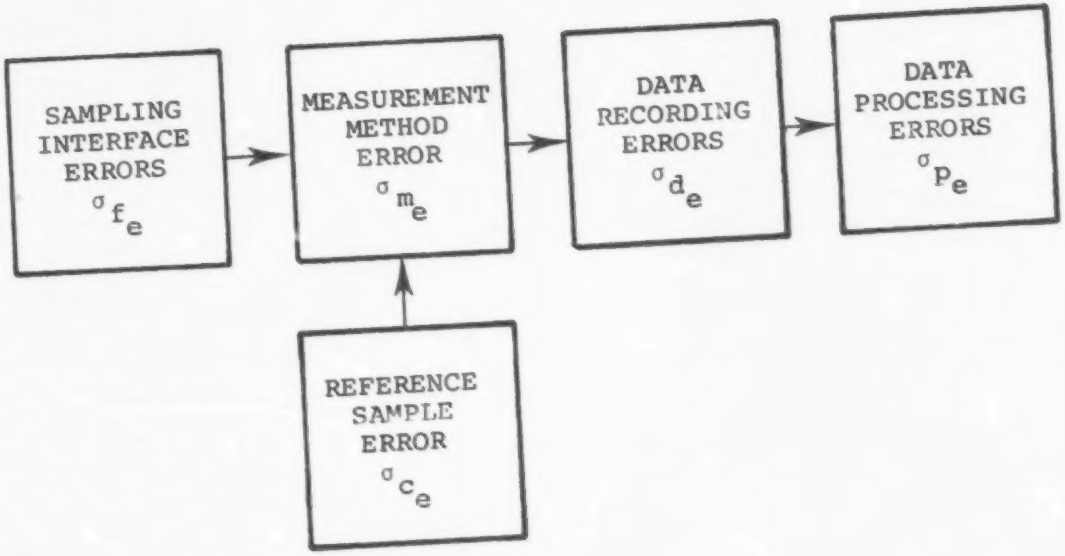

SAMPLING INTERFACE ERRORS σ_{f_e}
MEASUREMENT METHOD ERROR σ_{m_e}
DATA RECORDING ERRORS σ_{d_e}
DATA PROCESSING ERRORS σ_{p_e}
REFERENCE SAMPLE ERROR σ_{c_e}

Figure 5.11.15 Major components of system errors in an extractive monitoring system.

Obvious sources of error in most types of interface system include:

1. Loss of sample due to leaks or adsorption in the sampling probe or sample lines,
2. Malfunction of control valves,
3. Loss of sample in water vapor reduction technique,
4. Incorrect sample flow due to plugging by particulates which can occur through the use of ineffective filtering, failure to change filters at reasonable intervals, or incorrect positioning of the probe filter.
5. Inaccurately assumed dilution ratio if dilution system is used,
6. Improper operation of condensation or water vapor removal system which results in higher actual concentration of water vapor in sample entering analyzer than is assumed,
7. Improper maintenance of sample gas temperature compatible with the analyzer, and
8. Chemical reaction with interface construction materials.

Most of the above sources of error can be eliminated with a comprehensive operation and maintenance program designed to meet the requirements of the specific system in use (ref. 10). An estimated standard deviation (for illustrative purposes only) of the final measurement due to interface system errors, σ_{f_e}, is 10 percent of the actual sulfur dioxide concentration.

3.1.2.2 Measurement Method Errors, σ_{m_e}--Just as with the in-situ monitoring systems discussed in section 3.1.1.1, each of the analyzing techniques used in extractive monitoring systems have certain inherent error sources. Because of the wide variety of techniques this document will list only a few of these error sources which may or may not be applicable to all analyzers. The common error sources are:

1. Interferences by other constituents of the stack gas. Water vapor, nitric oxide, sulfuric acid, and hydrogen sulfides are some constituents of the stack gas which may interfere with the measurement of sulfur dioxide thereby reducing the specificity of the measurement method. Although this error source may be considered dependent upon the efficiency of the conditioning system with respect to the interfering species, it is assumed that the inefficiency of the conditioning system below specified limits contributes to σ_{f_e} and that those same specified limits are used in determining errors due to the sensitivity of the analyzer to the minimum amount of the interfering species which comes under σ_{m_e}. This assumption allows both error sources to be considered independent for purposes of variable analysis in this document.
2. Plugging of the internal sample lines. The flow rate through the analyzer can be hampered by undue plugging of the sample lines internal to the analyzer resulting from accumulation of particulate matter and water vapor beyond the minimum efficiency specifications of the interface components.
3. Improper operation of internal sample dryers. The malfunction of internal sample dryers not

compensated for with external components can cause interference above the amount adjusted for by the analyzer.

4. Initial setup and calibration of system. Discussions on the influence of setting up and calibrating a system at a large full-scale value relative to existing emission levels have shown that the analyzer accuracy can be greatly reduced (ref. 17).
5. Zero and calibration drift. Zero and span drift due to the analyzer's sensitivity to pressure and temperature changes between manual or automatic checks will alter the data accuracy. In most cases the drift is random and the data cannot be accurately adjusted based on subsequent calibration data.

An estimated (for illustrative purposes only) standard deviation of 8 percent of the true measurement value is used here for illustrative purposes as representative of the error due to the analysis technique.

3.1.2.3 Reference Sample Error, σ_{C_e}--The analysis of sulfur dioxide by extractive continuous monitors is subject to error from inaccuracies in the calibration gases used for either manual or automatic calibration and in the calibration technique. Most extractive measurement systems are calibrated with cylinder gas. Error in the assumed concentration value of the reference gas will result in a bias of the measurements for the lifetime of the cylinder. Error in the calibration technique is a function of the similarity between the pathway of the sample stack gas through the system and the pathway of the calibration gas. Ideally, the calibration gas should be input at the sample probe and, upon entering the analyzer, would go through the same internal sample lines to the final measurement cell.

The standard deviation of the true measurement value due to calibration error, σ_{c_e}, is estimated at 8 percent of the true measurement value.

3.1.2.4 Data Recording Errors, σ_{r_e}--As is the case with in-situ monitoring, data recording errors can result from inadequate response of the mechanical stripchart recorder to varying sulfur dioxide concentration. If magnetic tape recording systems are used, error in the recorded signal can result from improper amplification of the analyzer output or malfunctions in the recorder. Because of the advanced state-of-art in data acquisition systems, a standard deviation, σ_{r_e}, of 2 percent is estimated for the effects of data recording errors on the measurement of sulfur dioxide by an extractive monitor.

3.1.2.5 Data Processing Errors, σ_{P_e}--As with in-situ monitoring systems, data processing errors can be avoided through extreme conscientiousness of the data processing personnel. Errors may occur, though, in making accurate estimates of average values on illegible stripchart recordings. Other error sources are:

1. Misreading of calibration data from stripchart recording or raw magnetic tape recording data. This can take the form of data being read as span data when the system has not actually stabilized at a span reading.
2. Carelessness in reading discrete measurement values with the utmost accuracy.

3. Mistakes such as manually reading the correct data and transposing the numerical figures upon recording the data.
4. Calculation errors in determining average concentrations over an extended sampling period.
5. Time shifting of magnetic tape data resulting from improper input of start time data into the computer or from loss of data without battery carryover for recorder time synchronization with real time (the latter is also applicable to stripchart records).

An estimate of the standard deviation of the measurement value as a result of data processing errors, σ_{Pe}, is 3 percent.

3.1.2.6 Total Standard Deviation, σ_{T_e}--All of the error terms discussed above are independent, hence the total bias in the continuous measurement of sulfur dioxide by extractive monitors is the algebraic sum of the individual terms. The variance of the data, $\sigma_{T_e}^2$, is the sum of the variances of the individual error terms as follows:

$$\sigma_{T_e}^2 = \sigma_m^2 + \sigma_c^2 + \sigma_r^2 + \sigma_p^2 .$$

Using the estimated values given in the previous paragraphs, $\sigma_{T_e}^2 = .0183$ and $\sigma_{T_e} = 13.5$ percent of the true concentration of sulfur dioxide. This value is comparable to results from evaluations of several monitoring systems which range between 10 and 15 percent (see refs. 13 through 17).

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LIST OF REFERENCES

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APPENDIX A

Performance Specification 3—Performance specifications and specification test procedures for monitors of CO_2 and O_2 from stationary sources.

1. Principle and Applicability.

1.1 Principle. Effluent gases are continuously sampled and are analyzed for carbon dioxide or oxygen by a continuous monitoring system. Tests of the system are performed during a minimum operating period to determine zero drift, calibration drift, and response time characteristics.

1.2 Applicability. This performance specification is applicable to evaluation of continuous monitoring systems for measurement of carbon dioxide or oxygen. These specifications contain test procedures, installation requirements, and data computation procedures for evaluating the acceptability of the continuous monitoring systems subject to approval by the Administrator. Sampling may include either extractive or non-extractive (in-situ) procedures.

2. Apparatus.

2.1 Continuous Monitoring System for Carbon Dioxide or Oxygen.

2.2 Calibration Gas Mixtures. Mixture of known concentrations of carbon dioxide or oxygen in nitrogen or air. Midrange and 90 percent of span carbon dioxide or oxygen concentrations are required. The 90 percent of span gas mixture is to be used to set and check the analyzer span and is referred to as span gas. For oxygen analyzers, if the span is higher than 21 percent O_2, ambient air may be used in place of the 90 percent of span calibration gas mixture. Triplicate analyses of the gas mixture (except ambient air) shall be performed within two weeks prior to use using Reference Method 3 of this part.

2.3 Zero Gas. A gas containing less than 100 ppm of carbon dioxide or oxygen.

2.4 Data Recorder. Analog chart recorder or other suitable device with input voltage range compatible with analyzer system output. The resolution of the recorder's data output shall be sufficient to allow completion of the test procedures within this specification.

3. Definitions.

3.1 Continuous Monitoring System. The total equipment required for the determination of carbon dioxide or oxygen in a given source effluent. The system consists of three major subsystems:

3.1.1 Sampling Interface. That portion of the continuous monitoring system that performs one or more of the following operations: delineation, acquisition, transportation, and conditioning of a sample of the source effluent or protection of the analyzer from the hostile aspects of the sample or source environment.

3.1.2 Analyzer. That portion of the continuous monitoring system which senses the pollutant gas and generates a signal output that is a function of the pollutant concentration.

3.1.3 Data Recorder. That portion of the continuous monitoring system that provides a permanent record of the output signal in terms of concentration units.

3.2 Span. The value of oxygen or carbon dioxide concentration at which the continuous monitoring system is set that produces the maximum data display output. For the purposes of this method, the span shall be set no less than 1.5 to 2.5 times the normal carbon dioxide or normal oxygen concentration in the stack gas of the affected facility.

3.3 Midrange. The value of oxygen or carbon dioxide concentration that is representative of the normal conditions in the stack gas of the affected facility at typical operating rates.

3.4 Zero Drift. The change in the continuous monitoring system output over a stated period of time of normal continuous operation when the carbon dioxide or oxygen concentration at the time for the measurements is zero.

3.5 Calibration Drift. The change in the continuous monitoring system output over a stated time period of normal continuous operation when the carbon dioxide or oxygen continuous monitoring system is measuring the concentration of span gas.

3.6 Operational Test Period. A minimum period of time over which the continuous monitoring system is expected to operate within certain performance specifications without unscheduled maintenance, repair, or adjustment.

3.7 Response time. The time interval from a step change in concentration at the input to the continuous monitoring system to the time at which 95 percent of the corresponding final value is displayed on the continuous monitoring system data recorder.

4. Installation Specification.

Oxygen or carbon dioxide continuous monitoring systems shall be installed at a location where measurements are directly representative of the total effluent from the affected facility or representative of the same effluent sampled by a SO_2 or NO_x continuous monitoring system. This requirement shall be complied with by use of applicable requirements in Performance Specification 2 of this appendix as follows:

4.1 Installation of Oxygen or Carbon Dioxide Continuous Monitoring Systems Not Used to Convert Pollutant Data. A sampling location shall be selected in accordance with the procedures under paragraphs 4.2.1 or 4.2.2, or Performance Specification 2 of this appendix.

4.2 Installation of Oxygen or Carbon Dioxide Continuous Monitoring Systems Used to Convert Pollutant Continuous Monitoring System Data to Units of Applicable Standards. The diluent continuous monitoring system (oxygen or carbon dioxide) shall be installed at a sampling location where measurements that can be made are representative of the effluent gases sampled by the pollutant continuous monitoring system(s). Conformance with this requirement may be accomplished in any of the following ways:

4.2.1 The sampling location for the diluent system shall be near the sampling location for the pollutant continuous monitoring system such that the same approximate point(s) (extractive systems) or path (in-situ systems) in the cross section is sampled or viewed.

4.2.2 The diluent and pollutant continuous monitoring systems may be installed at different locations if the effluent gases at both sampling locations are nonstratified as determined under paragraphs 4.1 or 4.3, Performance Specification 2 of this appendix and there is no in-leakage occurring between the two sampling locations. If the effluent gases are stratified at either location, the procedures under paragraph 4.2.2, Performance Specification 2 of this appendix shall be used for installing continuous monitoring systems at that location.

5. Continuous Monitoring System Performance Specifications.

The continuous monitoring system shall meet the performance specifications in Table 3-1 to be considered acceptable under this method.

6. Performance Specification Test Procedures.

The following test procedures shall be used to determine conformance with the requirements of paragraph 4. Due to the wide variation existing in analyzer designs and principles of operation, these procedures are not applicable to all analyzers. Where this occurs, alternative procedures, subject to the approval of the Administrator, may be employed. Any such alternative procedures must fulfill the same purposes (verify response, drift, and accuracy) as the following procedures, and must clearly demonstrate conformance with specifications in Table 3-1.

6.1 Calibration Check. Establish a calibration curve for the continuous monitoring system using zero, midrange, and span concentration gas mixtures. Verify that the resultant curve of analyzer reading compared with the calibration gas value is consistent with the expected response curve as described by the analyzer manufacturer. If the expected response curve is not produced, additional calibration gas measurements shall be made, or additional steps undertaken to verify the accuracy of the response curve of the analyzer.

6.2 Field Test for Zero Drift and Calibration Drift. Install and operate the continuous monitoring system in accordance with the manufacturer's written instructions and drawings as follows:

TABLE 3-1.—*Performance specifications*

Parameter	*Specification*
1. Zero drift (2 h) [1]	≤0.4 pct O_2 or CO_2.
2. Zero drift (24 h) [1]	≤0.5 pct O_2 or CO_2.
3. Calibration drift (2 h) [1]	≤0.4 pct O_2 or CO_2.
4. Calibration drift (24 h) [1]	≤0.5 pct O_2 or CO_2.
5. Operational period	168 h minimum.
6. Response time	10 min.

[1] Expressed as sum of absolute mean value plus 95 pct confidence interval of a series of tests.

6.2.1 Conditioning Period. Offset the zero setting at least 10 percent of span so that negative zero drift may be quantified. Operate the continuous monitoring system for an initial 168-hour conditioning period in a normal operational manner.

6.2.2. Operational Test Period. Operate the continuous monitoring system for an additional 168-hour period maintaining the zero offset. The system shall monitor the source effluent at all times except when being zeroed, calibrated, or backpurged.

6.2.3 Field Test for Zero Drift and Calibration Drift. Determine the values given by zero and midrange gas concentrations at two-hour intervals until 15 sets of data are obtained. For non-extractive continuous monitoring systems, determine the zero value given by a mechanically produced zero condition or by computing the zero value from upscale measurements using calibrated gas cells certified by the manufacturer. The midrange checks shall be performed by using certified calibration gas cells functionally equivalent to less than 50 percent of span. Record these readings on the example sheet shown in Figure 3-1. These two-hour periods need not be consecutive but may not overlap. In-situ CO_2 or O_2 analyzers which cannot be fitted with a calibration gas cell may be calibrated by alternative procedures acceptable to the Administrator. Zero and calibration corrections and adjustments are allowed only at 24-hour intervals or at such shorter intervals as the manufacturer's written instructions specify. Automatic corrections made by the continuous monitoring system without operator intervention or initiation are allowable at any time. During the entire 168-hour test period, record the values given by zero and span gas concentrations before and after adjustment at 24-hour intervals in the example sheet shown in Figure 3-2.

6.3 Field Test for Response Time.

6.3.1 Scope of Test.

This test shall be accomplished using the continuous monitoring system as installed, including sample transport lines if used. Flow rates, line diameters, pumping rates, pressures (do not allow the pressurized calibration gas to change the normal operating pressure in the sample line), etc., shall be at the nominal values for normal operation as specified in the manufacturer's written instructions. If the analyzer is used to sample more than one source (stack), this test shall be repeated for each sampling point.

6.3.2 Response Time Test Procedure.

Introduce zero gas into the continuous monitoring system sampling interface or as close to the sampling interface as possible. When the system output reading has stabilized, switch quickly to a known concentration of gas at 90 percent of span. Record the time from concentration switching to 95 percent of final stable response. After the system response has stabilized at the upper level, switch quickly to a zero gas. Record the time from concentration switching to 95 percent of final stable response. Alternatively, for nonextractive continuous monitoring systems, the highest available calibration gas concentration shall be switched into and out of the sample path and response times recorded. Perform this test sequence three (3) times. For each test, record the results on the data sheet shown in Figure 3-3.

7. Calculations, Data Analysis, and Reporting.

7.1 Procedure for determination of mean values and confidence intervals.

7.1.1 The mean value of a data set is calculated according to equation 3-1.

$$\bar{x}=\frac{1}{n}\sum_{i=1}^{n}x_i \qquad \text{Equation 3-1}$$

where:

x_i = absolute value of the measurements,
Σ = sum of the individual values,
$\bar{x}$ = mean value, and
n = number of data points.

7.2.1 The 95 percent confidence interval (two-sided) is calculated according to equation 3-2:

$$C.I._{95}=\frac{t_{.975}}{n\sqrt{n-1}}\sqrt{n(\sum x_i^2)-(\sum x_i)^2} \qquad \text{Equation 3-2}$$

where:

ΣX = sum of all data points,
$t_{.975}=t_1-\alpha/2$, and
$C.I._{95}$ = 95 percent confidence interval estimated of the average mean value. value.

Values for $t_{.975}$

n	$t_{.975}$
2	12.706
3	4.303
4	3.182
5	2.776
6	2.571
7	2.447
8	2.365
9	2.306
10	2.262
11	2.228
12	2.201
13	2.179
14	2.160
15	2.145
16	2.131

The values in this table are already corrected for n-1 degrees of freedom. Use n equal to the number of samples as data points.

7.2 Data Analysis and Reporting.

7.2.1 Zero Drift (2-hour). Using the zero concentration values measured each two hours during the field test, calculate the differences between the consecutive two-hour readings expressed in ppm. Calculate the mean difference and the confidence interval using equations 3-1 and 3-2. Record the sum of the absolute mean value and the confidence interval on the data sheet shown in Figure 3-1.

7.2.2 Zero Drift (24-hour). Using the zero concentration values measured every 24 hours during the field test, calculate the differences between the zero point after zero adjustment and the zero value 24 hours later just prior to zero adjustment. Calculate the mean value of these points and the confidence interval using equations 3-1 and 3-2. Record the zero drift (the sum of the absolute mean and confidence interval) on the data sheet shown in Figure 3-2.

7.2.3 Calibration Drift (2-hour). Using the calibration values obtained at two-hour intervals during the field test, calculate the differences between consecutive two-hour readings expressed as ppm. These values should be corrected for the corresponding zero drift during that two-hour period. Calculate the mean and confidence interval of these corrected difference values using equations 3-1 and 3-2. Do not use the differences between non-consecutive readings. Record the sum of the absolute mean and confidence interval upon the data sheet shown in Figure 3-1.

7.2.4 Calibration Drift (24-hour). Using the calibration values measured every 24 hours during the field test, calculate the differences between the calibration concentration reading after zero and calibration adjustment and the calibration concentration reading 24 hours later after zero adjustment but before calibration adjustment. Calculate the mean value of these differences and the confidence interval using equations 3-1 and 3-2. Record the sum of the absolute mean and confidence interval on the data sheet shown in Figure 3-2.

7.2.5 Operational Test Period. During the 168-hour performance and operational test period, the continuous monitoring system shall not receive any corrective maintenance, repair, replacement, or adjustment other than that clearly specified as required in the manufacturer's written operation and maintenance manuals as routine and expected during a one-week period. If the continuous monitoring system operates within the specified performance parameters and does not require corrective maintenance, repair, replacement or adjustment other than as specified above during the 168-hour test period, the operational period will be successfully concluded. Failure of the continuous monitoring system to meet this requirement shall call for a repetition of the 168 hour test period. Portions of the test which were satisfactorily completed need not be repeated. Failure to meet any performance specifications shall call for a repetition of the one-week performance test period and that portion of the testing which is related to the failed specification. All maintenance and adjustments required shall be recorded. Output readings shall be recorded before and after all adjustments.

7.2.6 Response Time. Using the data developed under paragraph 5.3, calculate the time interval from concentration switching to 95 percent to the final stable value for all upscale and downscale tests. Report the mean of the three upscale test times and the mean of the three downscale test times. The two average times should not differ by more than 15 percent of the slower time. Report the slower time as the system response time. Record the results on Figure 3-3.

8. References.

8.1 "Performance Specifications for Stationary Source Monitoring Systems for Gases and Visible Emissions," Environmental Protection Agency, Research Triangle Park, N.C., EPA-650/2-74-013, January 1974.

8.2 "Experimental Statistics," Department of Commerce, National Bureau of Standards Handbook 91, 1963, pp. 3-31, paragraphs 3-3.1.4.

(Secs. 111 and 114 of the Clean Air Act, as amended by sec. 4(a) of Pub. L. 91-604, 84 Stat. 1678 (42 U.S.C. 1857c-6, by sec. 15(c)(2) of Pub. L. 91-604, 85 Stat. 1713 (42 U.S.C. 1857g)).

Data Set✓ No.	Time		Date	Zero Reading	Zero Drift (ΔZero)	Span Reading	Span Drift (ΔSpan)	Calibration Drift (ΔSpan-ΔZero)
	Begin	End						
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
11								
12								
13								
14								
15								

Zero Drift = [Mean Zero Drift* ________ + CI (Zero) ________] = ________.
Calibration Drift = [Mean Span Drift* ______ + CI (Span ______] = ________.
*Absolute Value.

Figure 3-1. Zero and Calibration Drift (2 Hour).

Date and Time	Zero Reading	Zero Drift (ΔZero)	Span Reading (After zero adjustment)	Calibration Drift (ΔSpan)

Zero Drift = [Mean Zero Drift* _______ + C.I. (Zero) _______]
= ________.

Calibration Drift = [Mean Span Drift* ________ + C.I. (Span) ________]
= ________.

* Absolute value

Figure 3-2. Zero and Calibration Drift (24-hour)

Date of Test ____________

Span Gas Concentration ________ ppm

Analyzer Span Setting ________ ppm

Upscale
1. ________ seconds
2. ________ seconds
3. ________ seconds

Average upscale response ________ seconds

Downscale
1. ________ seconds
2. ________ seconds
3. ________ seconds

Average downscale response ________ seconds

System average response time (slower time) = ________ seconds

$$\text{\% deviation from slower system average response} = \frac{\text{average upscale minus average downscale}}{\text{slower time}} \times 100\%$$

= ___________.

Figure 3-3. Response

[FR Doc.75-26568 Filed 10-3-75;8:45 am]

APPENDIX B

APPENDIX B

GLOSSARY OF SYMBOLS

This is a glossary of the symbols used in this document. Symbols used and defined in the reference method (section 5.11.1) are not repeated here.

λ_o	Given wavelength of light.
d_A	Difference between average measured concentration value of calibration gas A and the continuous measurement system reading during calibration error test.
d_B	Difference between average measured concentration value of calibration gas B and the continuous measurement system reading during calibration error test.
SUM 1	Sum of the d_A values determined in a calibration error test.
SUM 2	Sum of the squares of the d_A values ($d_A{}^2$) used in the calibration error calculation.
SUM 3	Sum of the d_B values determined in a calibration error test.
SUM 4	Sum of the squares of the d_B values ($d_B{}^2$) used in the calibration error calculation.
d_i	Difference between the reference method value (ppm) and the average analyzer measurement for the ith interval in an accuracy test.
$d_i{}^2$	Square of d_i value for ith interval.
SUM 5	Sum of the d_i values for nine accuracy test measurements.
SUM 6	Sum of the squares of the d_i values ($d_i{}^2$) used in a calculation of continuous system accuracy.
SUM 7	Sum of the reference method measurements determined in an accuracy test and used in the calculation of system accuracy.
ΔZ	Difference in zero reading from zero reading taken two hours before.
ΔZ^2	Square of ΔZ value.

C	Calibration drift calculated using the 2-hour span drift (ppm) minus the zero drift (ppm) for the corresponding time period.
C^2	Square of 2-hour calibration drift value.
SUM 8	Sum of the ΔZ values taken in a series of 2-hour zero drift tests.
SUM 9	Sum of the squares of the ΔZ values (ΔZ^2) taken in a series of 2-hour zero drift tests.
SUM 10	Sum of the calibration drift (C) values calculated from a series of calibration drift tests.
SUM 11	Sum of the squares of calibration drift values (C^2) calculated after a series of 2-hour calibration drift tests.
ΔZ_{24}	Difference in zero reading from zero reading taken 24 hours before.
$\Delta Z_{24}{}^2$	Square of the 24-hour zero drift value.
C_{24}	Calibration drift calculated using the 24-hour span drift (ppm) minus the zero drift (ppm) for the corresponding time period.
$C_{24}{}^2$	Square of the 24-hour calibration drift value.
SUM 12	Sum of the 24-hour zero drift values taken from a series of 24-hour drift tests.
SUM 13	Sum of the squares of the 24-hour zero drift values taken from a series of 24-hour zero drift tests.
SUM 14	Sum of the 24-hour calibration drift values.
SUM 15	Sum of the squares of the 24-hour calibration drift values ($C_{24}{}^2$).
SUM 16	Sum of the upscale response time measurement values (seconds).
SUM 17	Sum of the downscale response time measurement values (seconds).
n	Sample size for the auditing.
UCL	Upper quality limit determined from performance test data and used in assessment of routine calibration data.
LCL	Lower quality limit determined from performance test data and used in assessment of routine calibration data.

d_i	Difference between continuous system 1-hour average data minus the Method 8 value for the i^{th} measurement.
S_1	Sum of the differences (d_i) calculated from a series of Method 8 measurements compared with continuous system data.
S_2	Sum of the squares of the differences (d_i^2)
S_3	Sum of the reference method values calculated from a series of measurements.
$\bar{C}_R$	Mean reference method value calculated from audit data.
σ_m	Standard deviation of in-situ continuous method measurement due to measurement method errors.
σ_c	Standard deviation of continuous method measurement due to calibration inadequacies and the associated drift problems in in-situ monitoring systems.
σ_r	Standard deviation in in-situ measurement due to data recording errors.
σ_p	Standard deviation of in-situ measurement due to data processing errors.
σ_T	Standard deviation of the in-situ measurement which is a function of the component errors.
σ_{f_e}	Standard deviation of extractive system measurement due to sampling interface errors.
σ_{m_e}	Standard deviation of extractive continuous method measurement due to measurement method errors.
σ_{c_e}	Standard deviation of continuous method measurement due to calibration inadequacies and the associated drift problems in extractive monitoring systems.
σ_{r_e}	Standard deviation of extractive measurement due to data recording errors.
σ_{p_e}	Standard deviation of extractive measurement due to data processing errors.
σ_{T_e}	Standard deviation of the extractive measurement which is a function of the component errors.

APPENDIX C

APPENDIX C

GLOSSARY OF TERMS

The following glossary lists and defines the statistical terms as used in this document.

Accuracy	A measure of the error of a process expressed as a comparison between the average of the measured values and the true or accepted value. It is a function of precision and bias.
Bias	The systematic or nonrandom component of measurement error.
Lot	A specified number of objects to be treated as a group, e.g., the number of field tests to be conducted by an organization during a specified period of time (usually a calendar quarter).
Measurement method	A set of procedures for making a measurement.
Measurement process	The process of making a measurement, including method, personnel, equipment, and environmental conditions.
Population	The totality of the set of items, units, or measurements, real or conceptual, that is under consideration.
Precision	The degree of variation among successive, independent measurements (e.g., on a homogeneous material) under controlled conditions, and usually expressed as a standard deviation or as a coefficient of variation.
Quality audit	A management tool for independently assessing data quality.
Quality control check	Checks made by the field crew on certain items of equipment and procedures to assure data of good quality.
Sample	Objects drawn, usually at random, from the lot for checking or auditing purposes.